

# Synthesis of Polymers

Edited by A.-Dieter Schlüter

**Materials Science and  
Technology Series**

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**R. W. Cahn,**  
**P. Haasen,**  
**E. J. Kramer**



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## **Synthesis of Polymers**

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# **Materials Science and Technology**

**A Comprehensive Treatment**

Edited by

**R.W. Cahn, P. Haasen, E.J. Kramer**

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**Synthesis of Polymers**

**Volume Editor: A.-Dieter Schlüter**

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## Preface to the Series

Materials are highly diverse, yet many concepts, phenomena and transformations involved in making and using metals, ceramics, electronic materials, plastics and composites are strikingly similar. Matters such as transformation mechanisms, defect behavior, the thermodynamics of equilibria, diffusion, flow and fracture mechanisms, the fine structure and behavior of interfaces, the structures of crystals and glasses and the relationship between these, the motion or confinement of electrons in diverse types of materials, the statistical mechanics of assemblies of atoms or magnetic spins, have come to illuminate not only the behavior of the individual materials in which they were originally studied, but also the behavior of other materials which at first sight are quite unrelated.

This continual intellectual cross-linkage between materials is what has given birth to *Materials Science*, which has by now become a discipline in its own right as well as being a meeting place of constituent disciplines. The new Series is intended to mark the coming-of-age of that new discipline, define its nature and range and provide a comprehensive overview of its principal constituent themes.

*Materials Technology* (sometimes called Materials Engineering) is the more practical counterpart of Materials Science, and its central concern is the processing of materials, which has become an immensely complex skill, especially for the newer categories such as semiconductors, polymers and advanced ceramics but indeed also for the older materials: thus, the reader will find that the metallurgy and processing of modern steels has developed a long way beyond old-fashioned empiricism.

There exist, of course, other volumes and other series aimed at surveying these topics. They range from encyclopedias, via annual reviews and progress serials, to individual texts and monographs, quite apart from the flood of individual review articles in scientific periodicals. Many of these are essential reading for specialists (and those who intend to become specialists); our objective is not to belittle other sources in the cooperative enterprise which is modern materials science and technology, but rather to create a self-contained series of books which can be close at hand for frequent reference or systematic study, and to create these books rapidly enough so that the early volumes will not yet be badly out of date when the last ones are published. The individual chapters are more detailed and searching than encyclopedia or concise review articles, but less so than monographs wholly devoted to a single theme.

The Series is directed toward a broad readership, including not only those who define themselves as materials scientists or engineers but also those active in diverse disciplines such as solid-state physics, solid-state chemistry, metallurgy,

construction engineering, electrical engineering and electronics, energy technology, polymer science and engineering.

While the Series is primarily classified on the basis of types of materials and their processing modes, some volumes will focus on particular groups of applications (Nuclear Materials, Biomedical Materials), and others on specific categories of properties (Phase Transformations, Characterization, Plastic Deformation and Fracture). Different aspects of the same topic are often treated in two or more volumes, and certain topics are treated in connection with a particular material (e.g., corrosion in one of the chapters on steel, and adhesion in one of the polymer volumes). Note, however, that corrosion is now to receive its own dedicated volume, number 19. Special care has been taken by the Editors to ensure extensive cross-references both within and between volumes, insofar as is feasible. A Cumulative Index volume will be published upon completion of the Series to enhance its usefulness as a whole.

We are very much indebted to the editorial and production staff at VCH for their substantial and highly efficient contribution to the heavy task of putting these volumes together and turning them into finished books. Our particular thanks go to Dr. Peter Gregory and Deborah Hollis on the editorial side and to Wirt.-Ing. Hans-Jochen Schmitt on the production side. We are grateful to the management of VCH for their confidence in us and for their steadfast support.

Robert W. Cahn, Cambridge  
Peter Haasen, Göttingen  
Edward J. Kramer, Ithaca

Our friend and coeditor-in-chief, Peter Haasen, fell ill in May and died in Göttingen on 18 October 1993, at the age of only 66. Nearly until the end, driven by conscience and his love of science, he continued to discharge his editorial functions for our joint enterprise and also for another in which he was engaged. His death represents a devastating loss to his family, to which he was so deeply devoted, to his colleagues, to his church, and to the worldwide professions of metal physics and physical metallurgy (which he regarded as closely related but by no means identical).

Dr. Haasen, who had been professor of metal physics at the University of Göttingen for more than three decades until his retirement in 1992, possessed a name to conjure with on both sides of the Atlantic. In his native Germany he was greatly influential, both on the public scene and among his students, who looked to him for wise counsel even when their own hair became speckled with gray. He was an editor of *Zeitschrift für Metallkunde*, was for a time president of the

Göttingen Academy of Arts and Sciences, was a central figure in the councils of the Deutsche Gesellschaft für Metallkunde (latterly, Materialkunde), a member of the Academia Europaea and a foreign member of the U.S. National Academy of Engineering.

In 1986, he took the first initiatives which led directly to the publisher's decision to create the 18 volumes of *Materials Science and Technology*, and he personally edited the first volume to appear, devoted to Phase Transformations and published in 1991; it has already won much praise. We, the undersigned, owe to him our own involvement in this great enterprise. We shall miss him immensely, and we shall honor his memory by doing our part to bring the enterprise to a successful conclusion.

Robert W. Cahn, Cambridge  
Edward J. Kramer, Ithaca  
October 1993



## Foreword

Almost seventy-five years have elapsed since Staudinger's formal introduction of the hotly debated topic of "high molecular" substances at a scientific meeting in Düsseldorf. Since that time polymer chemistry has come of age and, by the 1960s, many thought that the field was so mature that few important discoveries remained to be made.

This new volume, edited by A.-Dieter Schlüter, illustrates some of the many changes that continue to revolutionize the vibrant field of polymer synthesis. A quick survey of the list of contributors to this timely volume reveals that the authors are not only experts in organic and polymer synthesis but also fully conversant with fields as varied as organometallic chemistry, supramolecular chemistry, molecular biology, and enzymology. Therefore, it is not surprising that this volume does not attempt to gather all the important recent advances in the field of polymer synthesis. Instead, it has selected some of the latest and most promising modern methods of polymer synthesis to illustrate the wealth of synthetic approaches that keep this discipline at the forefront.

While established polymerization routes such as the Ziegler-Natta polymerization of olefins continue to be of prime importance, a number of other metal-catalyzed polymerization processes have also gained practical significance. Metathesis polymerization, both acyclic and ring-opening, has benefited from the great strides made in organometallic chemistry and a better fundamental understanding of the key processes that control polymer synthesis. "Classical" polymerization processes – anionic, cationic, and free radical – have also evolved considerably as our ability to use active species with more "covalent character" and better designed initiating and propagating systems has been enhanced.

As our array of synthetic tools grows, so does our ability to "engineer" macromolecules through the control of their architecture, the mode of their assembly, or the methods involved in their polymerization. For example, efficient methods have emerged for the preparation of cyclic, dendritic, topological, or double-stranded macromolecules – all within the past two decades. The interface of chemistry and biology that has revolutionized modern organic chemistry has also led to significant inroads in the design of biologically inspired macromolecules. Major advances have been made in the use of the techniques of both biotechnology and molecular biology for the design and preparation of new families of macromolecules. The interface with inorganic chemistry has also led to novel hybrid polymers with great potential in areas as varied as nanoscale materials and catalysis. Explorations in the use of supramolecular chemistry, modular approaches, or repetitive organic techniques have also significantly expanded our ability to

conceive and realize novel macromolecular structures. Even a casual reader of this volume will not fail to be impressed by the richness of approaches to new macromolecules and the dynamic creativity that permeates polymer science today.

Jean M.J. Fréchet, Berkeley,  
November 1998

## Preface

Instead of attempting a comprehensive coverage of all aspects in polymer synthesis' broad field, we decided to emphasize areas and facets which have seen the most rapid development in the last few years. The topics chosen also reflect the organic chemist's preferences for mechanisms, structure control and elucidation of the synthesized polymers rather than their undoubtedly equally important materials properties. With its occasional NMR-spectrums and discussions of details such as defect degrees in polymer backbones this book acts as a perfect complement to related books currently on the market which tend to concentrate more on polymer's material science aspects. The selection of topics in this book also mirrors our appreciation for and belief in the impact of a boundary breaking, multi-disciplined interaction between chemistry/biochemistry scientists. Since polymer synthesis is an internationally pursued enterprise, it comes as no surprise that the renowned authors of the individual chapters hail from the leading nations in this field which are predominantly Europe, USA, and Japan. The targeted group of readers ranges from senior graduate students to academic and industrial researchers alike who seek exposure to advanced and modern aspects of polymer synthesis.

At this point I wish to cordially thank my former mentors, Gerhard Wegner and Henry Hall Jr., for igniting my enthusiasm for polymers and for pulling me over from straight organic chemistry to the fascinating world of the long and coily molecules.

A.-Dieter Schlüter, Berlin,  
November 1998



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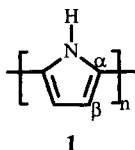
# Organic Chemistry and the Synthesis of Well-Defined Polymers

Klaus Müllen

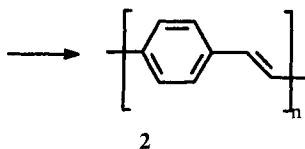
Max-Planck-Institut für Polymerforschung, Mainz, Germany

Organic chemists tend to avoid polymers and are happy when “polymers” remain at the top of their chromatography column. They consider polymers somewhat mysterious and the people who make them somewhat suspect. Polydisperse samples are not accepted as “true” compounds and it is believed that a method of bond formation, once established for the synthesis of a small compound, can be extended without further complication toward polymer synthesis. On the other hand, many polymer researchers, in particular those closer to the physical side of the field, have not invested much to increase trust in the structural homogeneity of their samples.

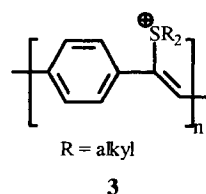
Some examples taken from the field of conjugated polymers may characterize this careless attitude. While electrochemically formed polypyrrole (MacDiarmid, 1997) is generally referred to by the idealized chain structure **1**, its actual structure is much more



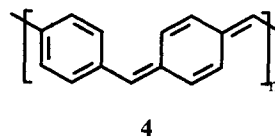
complex and comprises coupling at C- $\beta$  as well as ring-forming processes. Similarly, while poly(*para*-phenylenevinylene)s (**2**)



(PPVs) (Shinar, 1996) have been made readily available through the Wessling-Zimmerman route (Wessling and Zimmerman, 1986) using the precursor polyelectrolyte **3**,



a careful chemical approach was required to find the best conditions for the elimination upon going from **3** to **2**. A failure in this reaction will interrupt the extended  $\pi$ -conjugation, and side products can seriously affect the performance of, e. g., light-emitting devices made from **2** (Brown et al., 1992). Other structures, such as the polyphenyleneemethide **4**, with a degenerate ground-



state and, hopefully (Scherf and Müllen, 1992), a low electronic band gap, may represent a wish rather than reality, because once formed they are susceptible to chemical reactions producing structural defects.

These cases should suffice to outline the dilemma of a chemistry strongly biased toward physical function and material properties: While a synthesis must be “practical” and provide sufficient quantities, the limi-

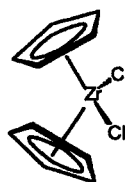


tations of the synthetic method, with respect to the occurrence of side products and structural defects, must be carefully investigated, e. g., for establishing a reliable structure-property relationship.

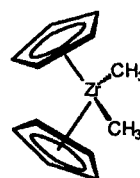
The last fifteen years have seen impressive cases where methods of organic and organometallic chemistry have been successfully implemented into polymer synthesis and largely increased the efficiency. Regio- and stereoselectivity, molecular weight control and access to more complex architectures of both homo- and copolymers have been among the major concerns of this research. Interdisciplinary approaches appeared to be particularly fruitful, and the literature provides ample examples where researchers have been stimulating exchange between seemingly closed communities. The present text, while being intended to highlight a few examples of creative polymer synthesis, is far from being comprehensive; methods of organometallic chemistry will certainly demand particular attention, above all in catalyzed processes of polymerization and polycondensation. Progress in polymer synthesis, on the other hand, does not only come from the invention of new reactions, but also from better solutions for old processes. Thus successful approaches toward "living" radical polymerization have led to a renaissance of classical polymer chemistry (Hawker, 1996). Seemingly fashionable topics, however, attract contributions of diverse quality and a situation close to chain death is sometimes looked at as a degree of "livingness". A final aspect when reviewing new avenues of polymer chemistry is not method-oriented, but will comprise the design and synthesis of unconventional structures.

It is appropriate to begin with the synthetic polymer that we make most of, that is, polyethylene. The story began in 1933 when a fairly ill-defined, i. e., branched, material

was produced in a high pressure/high temperature process (Seymour and Cheng, 1986). In the 1950s Ziegler-Natta catalysts led to highly linear polyethylene (Ziegler, 1952), and the polymerization of propylene (Natta, 1964) was successful with these catalysts as well. In the 1980s the use of sophisticated metallocenes as homogeneous (in contrast to polymer-supported Ziegler-Natta) catalysts allowed more and more control of polyolefin structures and properties (Brintzinger et al., 1995; Mühlhaupt, 1993). The activation of such catalysts with alkylaluminum compounds supported the conclusion that (alkyl) metallocene cations are key intermediates in ethylene polymerization. A particularly striking example is the activation of  $(\text{Cp})_2\text{ZrCl}_2$  (**5**) or  $(\text{Cp})_2\text{ZrMe}_2$  (**6**) complexes with methylalumin-



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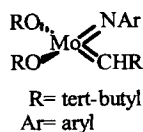
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oxane (MAO), which was introduced by Sinn et al. (1980). Extensive kinetic and theoretical studies disclosed a mechanism in which the productive complex is an alkyl (olefin) zirconocene cation and the olefin insertion into the metal-alkyl bond is the key step (Bochmann and Lancaster, 1992).

The detection of homogeneous catalysts also allowing the polymerization of propylene and other  $\alpha$ -olefins, fueled interest in the polymerization's stereoregularity and its relation to the substitution pattern of the metallocene. It is thus the geometric and electronic structure of tailor-made metallocenes that determines the structure of the resulting polymer chain and its properties, such as crystallinity, transparency, stiffness, or heat resistance (Brintzinger et al., 1995;

Mühlhaupt, 1993). It should be added that the implementation of “homogeneous” catalysis in industrial polyolefin synthesis again requires the design of suitable carriers for the catalysts. While this might appear as a rather technical problem, its solution calls for a combination of synthetic, kinetic, analytical, and morphological efforts.

It may seem somewhat odd to proceed from the large-scale production of polyolefins to the synthesis of polyacetylene, a functional, “electrical” material, but the evolution of the methods is similar. Polyacetylene films were originally prepared via organometal-catalyzed polymerization of acetylene at interfaces (Shirakawa and Ikeda, 1971). Careful optimization of this process provided control of not only the molecular structure, but also the morphology of the solid, and thus led to impressive electrical conductivities, well comparable to those of copper. The major drawback of these materials was their intractability. In 1979 Feast introduced a precursor route in which a soluble precursor polymer was made via a ring opening metathesis polymerization (ROMP) using a  $\text{WCl}_4/\text{Sn}(\text{CH}_3)_4$  initiator, and in which the target polymer was obtained by a thermally induced elimination (Edwards and Feast, 1980). This first material was largely amorphous and no molecular weight control was possible. The use of carefully designed Schrock catalysts (**7**) al-

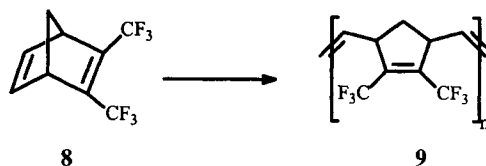


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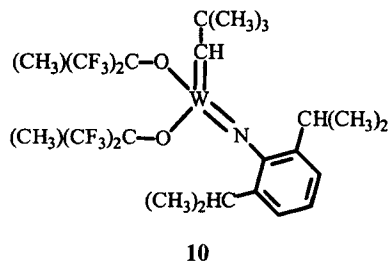
lowed a living polymerization and then enabled control of the molecular weight distribution and even the formation of block copolymers (Schrock et al., 1995).

Applying the ROMP process to other cycloolefins provided access to a manifold of

well-defined novel polymer structures. The chemical nature of the alkoxy or aryloxy ligands at the Schrock initiators led to highly tactic products and either *cis*- or *trans*-olefins in the transformation of the norbornadiene **8** into **9** (McConville et al., 1993; O'Dell et al., 1994).



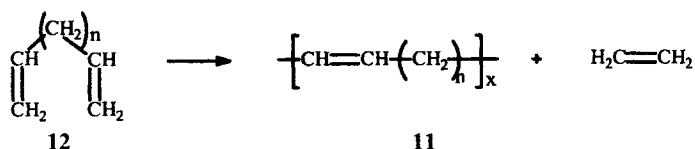
The success in the structural control of the polynorbornenes can be attributed to the deactivation of the electrophilic metal toward metathesis of ordinary olefins by the bulky alkoxy or aryloxy ligands in the catalyst **10**, to the selection of the less electro-



**10**

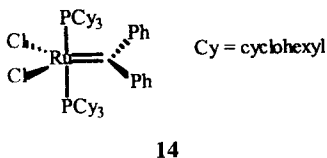
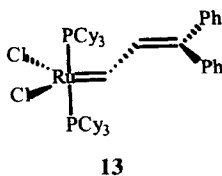
philic molybdenum compared to tungsten, and to the relatively high reactivity of the norbornene double bond (Bazan et al., 1991). Remarkably enough, the structural control reached by ROMP also allowed the synthesis of functional homo- and copolymers and their selective attachment to surfaces by their end function (Albagli et al., 1993), as well as the synthesis of new macromolecular architectures, such as star block copolymers and rod-coil block copolymers (Saunders et al., 1991).

Metathesis catalysts can also lead to chain structures, such as **11**, starting from  $\alpha, \omega$ -alkadiene precursors **12**, under the extrusion of ethylene in a process called acyclic diene metathesis (ADMET) (Wagener et al.,



1990). The removal of one low boiling product is crucial for driving the well-known equilibria of olefin metathesis with metal-locyclobutanes as key intermediates toward polymer formation.

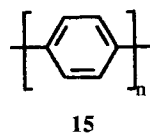
Finally, the novel ruthenium complexes **13** and **14**, recently introduced by Grubbs,



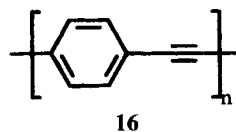
allow a living ROMP process of functionalized monomers in water (Lynn et al., 1996), a procedure that would have been believed impossible, e. g., five years ago. The living ends of the growing polymer chain are so persistent that the choice of the end-capping reagent is quite limited. This situation is in marked contrast with that of the living anionic polymerization of activated olefins (see below) where scrupulous exclusion, e. g., of proton sources, is mandatory in order not to disturb end-capping with electrophilic functions.

Organometal species do not only act as catalysts for polymerization, but also as key intermediates in polycondensation reactions under C-C bond formation. These reactions, such as Suzuki (Miyaura et al., 1981), Stille (Stille, 1986), or Heck (Heck, 1981) coupling, were designed for the syn-

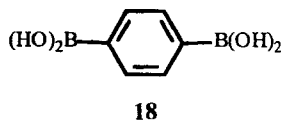
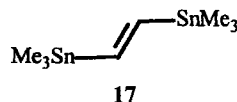
thesis of low molecular weight organic components and then, after having shown their value in repetitive processes, were shown by the fundamental work of Schlüter and Heitz to greatly improve the access to conjugated polymers such as polyphenylenes (PPPs) **15**



(Liess et al., 1996), polyphenylenevinylenes (PPVs) **2** (Klingelhöfer et al., 1997), or polyphenyleneethynylenes (PPEs) **16** (Koch and Heitz, 1997).

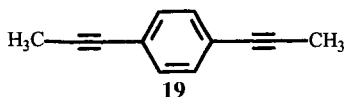


Crucial steps are aryl-aryl, aryl-vinyl, or aryl-ethynyl coupling, involving building blocks such as **17** or **18**, and proceeding



under palladium catalysis. Side reactions, such as dehalogenation or destannylation, must be strictly avoided, since they create an unbalanced stoichiometry and limit the attainable molecular weight. This often requires careful optimization of the reaction conditions and tuning of the catalyst system.

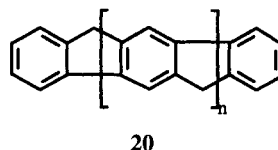
Interestingly, PPEs cannot only be made by aryl-ethynyl coupling, but also by a modification of the ADMET reaction (see earlier) using Schrock catalysts. The process uses dialkynyl substituted benzenes **19** as start-



ing compounds and is driven by butyne extrusion. During such a transfer of organic chemistry methods to polymer synthesis, the synthesis of oligomeric model compounds, either by a stepwise or random approach, and a scrupulous analysis of the products are of great value.

Next to the strict avoidance of structural errors, the construction of conjugated polymers faces the problems of improving the solubility of the rigid chains and controlling the electronic properties. As in PPV synthesis (see above), the problem of the poor solubility of poly(*para*-phenylene) (PPP) **15** was approached by making soluble precursor polymers, starting from solubilized cyclohexadiene monomers. The precursors can be smoothly transformed into the final conjugated PPP by elimination processes, but the perfection of this final transformation is again a critical theme (Chaturvedi et al., 1993). Otherwise, the introduction of solubilizing alkyl or alkoxy chains provided solubilized PPPs and, according to Wegner and Schlüter, the substituents do not seriously inhibit the Suzuki-type aryl-aryl cross coupling reaction (Percec et al., 1992; Rehahn et al., 1989). However, the substituents induce an increased mutual distortion of the inter-ring single bonds, and thus lead to severe inhibition of the resonance (Park et al., 1996). A pathway circumventing this shortcoming generates planarized PPPs by incorporating the conjugated PPP skeleton into a ladder geometry. The synthesis of perfectly flat and nevertheless solution-pro-

cessable PPPs was achieved with the synthesis of ladder poly(*para*-phenylene)s (LPPPs) **20** by Scherf and Müllen (1991).



Remarkably enough, such ladder polymers become available by carefully optimized polymer-analogous Friedel-Crafts cyclization, transforming single-stranded precursors into their defect-free, double-stranded counterparts.

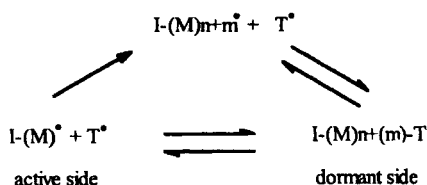
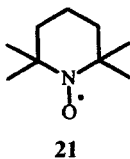
Unlike, e. g., polycondensation reactions of organometallic intermediates or metathesis polymerizations with sophisticated catalyst systems, the anionic, cationic, or radical polymerizations of activated olefins through chain processes are generally looked upon as classical topics of polymer chemistry. A key concern, e. g., in the anionic process, is the living character of the growing carbanion and the type of the metal counterion. While the living anions are typically generated by organolithium species, some polymerization reactions, such as the formation of polyethyleneoxide, require organopotassium initiators (Swarc and Van Beylen, 1993). It appears that the arguments describing the bonding situation of metal-stabilized carbanions are equally valid for organic and macromolecular chemistry. In general, the reactivity of the initiator has to be well tuned to prevent side reactions, especially in the case of block copolymer formation. For example, polystyrene-PMMA block copolymers cannot be obtained by the direct addition of MMA as the second monomer to the living polystyrene anions, since the high nucleophilicity of the polymeric anion would lead to an ester cleavage in the MMA (Young et al., 1984). An addition of diphenylethylene, however,

produces a less reactive polymeric anion and suppresses the side reactions with MMA.

New polymerization processes have recently been proposed, which are closely related to the classical anionic polymerization of acrylates. The focus is on the stabilization of ester enolates. Webster introduced the group transfer polymerization (Webster, 1987) using silylenol ethers and Yasuda described the polymerization of acrylates, initiated by complexes of alkylanthanium and -samarium (Ihara et al., 1995). With these methods, extremely narrowly distributed polymers were made accessible, and the tacticity of PMMA could even be controlled by using chiral complex ligands.

The major problem of anionic polymerization is the labor that needs to be invested in order to keep the carbanionic species unobstructed. Not surprisingly, therefore, polyacrylates or methacrylates are mostly prepared via the less demanding radical polymerization; thereby, however, complex architectures, such as block copolymers, are difficult to achieve. Here again, metal catalysis can play a central role. Copper complexes or ruthenium salts were applied by Matyjaszewski (Qiu and Matyjaszewski, 1997) and Sawamoto (Sawamoto and Kamigaito, 1996) to polymerize vinylic monomers in a controlled fashion. Thus high molecular weights and block copolymers were made. The disadvantage is that appreciable amounts of inorganic salts and/or complex ligands are involved, rendering this process difficult for an industrial application.

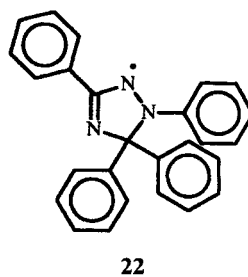
The second approach to obtain block copolymers uses counter radicals, such as stable nitroxides, mainly TEMPO **21**, as ad-



I = initiator, M = monomer, T = TEMPO **21**, triazolinyl **22**

ditives in radical polymerization (Rizzardo, 1987; Georges et al., 1993). The concentration of the growing macroradical can be largely reduced, which helps to suppress bimolecular side reactions.

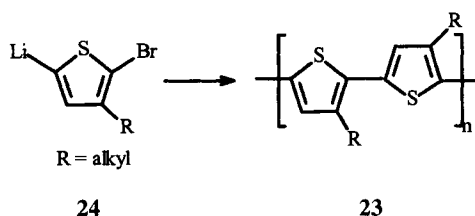
Unfortunately, stable nitroxides only allowed the polymerization of special monomers such as styrene. Fukuda (Goto and Fukuda, 1997) has suggested that the above-mentioned side reactions of free radicals cannot be completely suppressed by using additives. This will result in an increase of the concentration of counter radicals and shift the equilibrium between dormant and active species to the dormant side (see Scheme). Klapper and Müllen have introduced triazolinyl radicals (Colombani et al., 1997) **22** as counter radicals. Via controlled



decomposition of the latter, the concentration of the excess triazolinyl, formed via bimolecular side reactions of the polymerization, is decreased and, at the same time, new growing chains are initiated without the need for thermal reinitiation.

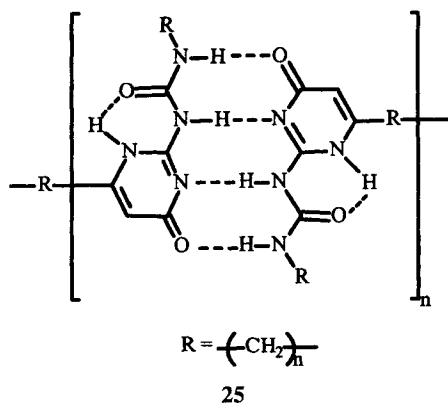
The above examples have generally dealt with activating monomers for polymerization, in particular, via C-C-bond formation,

and with achieving structural control at different levels of sophistication. Another impact of fundamental chemistry on polymer synthesis is the introduction of less common monomers. This is, of course, a vast field out of which only the functionalization and subsequent polymerization of fullerenes (Gügel et al., 1996) and the synthesis of regioregular poly(3-alkylthiophenes) **23** using McColloughs' AB building block **24** (McCollough et al., 1995) will be mentioned here.



Most of the synthetic methods mentioned so far revolve around the concept of a linear backbone made up of covalent bonds. A first departure from this classical path has been suggested with the involvement of noncovalent bonding, an approach that has been strongly advocated by Lehn (1993) and which resulted in the formation of polymeric hydrogen bonded aggregates or of polymeric coordination complexes. Major drawbacks of the "synthetic" use of hydrogen bonding have been the demanding syntheses of suitable monomeric building blocks and the formation of difficult-to-characterize solid products. Meijer has recently introduced a readily available monomer, which can activate four hydrogen bonds, thus leading to extremely high equilibrium constants of, e.g., dimerization. Coupling two such units through suitable spacers provides excess to the soluble high molecular weight polymers **25** (Meijer, 1997).

A characteristic property of flexible linear macromolecules is that they drastically change their overall extension in space by conformational interconversions. This spa-



tial extension can be reduced by changing the basic construction pattern. Accordingly, a second deviation from the classical polymer chain motif, next to noncovalent bonding, comes from the design of unconventional topologies such as large rings, stars, or dendrimers. Kricheldorf has used dioxastannanes as initiators for the efficient polymerization of  $\beta$ -butyrolactones to yield macrocyclic lactones (Kricheldorf and Lee, 1995). A more significant reduction of the mean-square dimensions of linear chains is produced in star-branch polymers. Convincing examples have been presented by Hajichristidis, who made complex architectures such as star block copolymers (Sioula et al., 1997). Thereby different arms, such as polystyrene and polyisoprene, were synthesized separately by anionic polymerization and the living macroanions linked together using dichlorosilanes as coupling elements.

Closely related to macrocycle formation is the use of topological bonds, like those occurring in polyrotaxanes **26** (Gibson et al., 1997) or polycatenanes **27**.



While the pioneering catenane synthesis of Schill and Lüttringhaus (1964) only led

to very small yields, impressive contributions of researchers, such as Stoddart (Ashton et al., 1997), Sauvage (Cardenas et al., 1997), Hunter (1995), and Vögtle (Ottens-Hildebrandt et al., 1995), have provided catenanes in such quantities that they could be used in polycatenane synthesis (Muscat et al., 1997). The originality of poly[2]-catenanes arises on the one hand from the introduction of topological bonds in the main chain, i. e., the repeating units are mechanically connected, and on the other from the new rotational and elongational elements of mobility contained in the catenane units. Polyrotaxanes can be viewed as elegant macromolecules dressed with macrocyclic necklaces, which are obtained by the threading of rings by growing polymer chains. Polyrotaxanes are relevant for a variety of purposes, such as studies in material science or the synthesis of tubular polymers, but also represent a particular type of blends whose behavior deviates strongly from the physical behavior of the individual components.

As is well known, the collapse of a chain toward a globular shape can be brought about by solvent effects. A synthetic equivalent of this process comes from the construction of highly branched molecules. Dendrimers (Zeng and Zimmermann, 1997; Tomalia et al., 1990) are the perfect monodisperse case, while their structurally less defined hyperbranched analogs represent the polydisperse case (Malmström and Hult, 1997). The remarkable role of dendritic structures for the creation of shape-persistent macromolecules and for the understanding of their "surface properties" is beyond the scope of this text. In this survey of adventures in polymer synthesis, it must, however, be emphasized that the repetition of branching steps using  $AB_n$ -type building blocks and the manipulation of highly functionalized molecular entities require an

enormous degree of reaction control. Also, it is highly appropriate in this context to point out the key role of new polymer analytical methods, such as MALDI-TOF (matrix assisted laser desorption ionization-time of flight) mass spectrometry, which are able to detect even minor structural defects (Spickermann et al., 1996). Dendrimers thus represent an ideal case to conclude a text devoted to the crucial role of synthesis in tailoring material properties.

Polymer scientists feeling closer to "classical" structures and to sound bread-and-butter chemistry might tend to consider, e. g., polycatenanes or dendrimers as somewhat exotic species requiring nonpractical and too sophisticated methods of synthesis. It cannot be stressed enough, however, that such synthetic efforts provide access to fundamental questions of polymer science. Whatever degree of complexity or simplicity is intended with a polymer synthesis, structural precision and control of multiple chemical functions are indispensable ingredients.

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# **1 Nonbiological Sequence-Specific Oligomers by Repetitive Syntheses**

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## List of Symbols and Abbreviations

<i>n</i>	number
BOC	<i>t</i> -butoxycarbonyl
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DMF	<i>N,N</i> -dimethylformamide
DNA	deoxyribonucleic acid
DNO	diamino acid- <i>N</i> -substituted oligopeptide
DNP	2,4-dinitrophenyl hydrazone
EG	end group
Et	ethyl
Fmoc	9-fluorenylmethoxy carbonyl
HBTU	2-(1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate
HPLC	high performance liquid chromatography
Me	methyl
NMP	<i>N</i> -methylpyrrolidine
NMR	nuclear magnetic resonance
NVOC	6-nitroveratryl methoxycarbonyl
Pg	protecting group
PNA	polyamide nucleic acid
RNA	ribonucleic acid
rt	room temperature
RU	repeat unit
THF	tetrahydrofuran

## 1.1 Introduction

Oligomers, as a member of the family of chemical substances, have perhaps suffered from the “syndrome of the middle child”. Like the recognition-deprived middle child, oligomers have not captured the level of interest that has been given to their polymeric “big sibling” or their small molecule “little sibling counterparts”. Nonetheless, from a historical perspective, it is easy to find examples where oligomers have provided invaluable understanding in linking the behavior of small molecule substances to macromolecules. Very recently, however, there has been renewed interest in the field of oligomer chemistry (Uglea and Negulescu, 1991; Tour, 1996), especially with regards to structurally defined substances prepared by repetitive syntheses (Moore, 1993). These compounds are shedding light in areas such as the supramolecular chemistry of macromolecules (e.g., protein-like folding) and they are now being recognized for their importance in fields such as medicinal chemistry and molecular biology, as well as for the continued understanding that they provide when addressing questions in polymer physical chemistry.

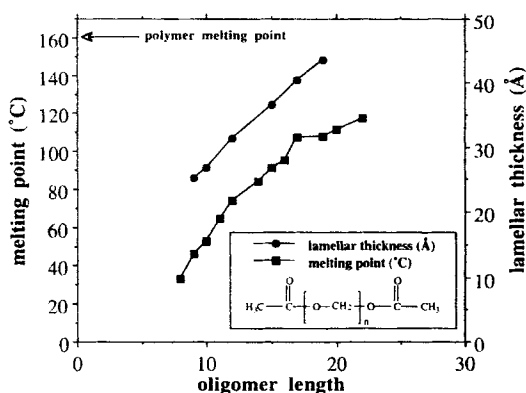
The term oligomer is compounded from the Greek prefix *olígos* meaning few and the Greek combining form *méros* meaning part. The general use of this term (Morawetz, 1985) apparently dates back to 1943 and is attributed to Larsen (1984). However, the terms “oligosaccharide” (Helferich et al., 1930) and “oligopeptide” (Helferich and Grünert, 1940) are recorded in the German literature by Helferich as early as 1930 and 1940, respectively.

Following a brief historical perspective which highlights the role of oligomers in substantiating Staudinger’s macromolecular hypothesis, an overview of repetitive synthetic strategies used in modern oligom-

er syntheses will be provided. Next, many examples of the descriptive chemistry used to prepare well-defined series of oligomers by repetitive methods will be presented. Excluded from this discussion are the naturally occurring oligomers (i.e., oligopeptides, oligonucleotides, and oligosaccharides), since these areas of chemistry are highly developed and specialized fields in themselves. The final section describes some examples that illustrate recent uses of oligomers in the design of controlled molecular architectures for materials and biological applications.

## 1.2 Bridging the Gap from Small Molecules to Macromolecules: A Brief Historical Sketch

While there can be no questioning the importance of synthetic polymeric materials, it is worth remembering that these substances are chemical mixtures, and mixtures are fundamentally different from pure substances. In many ways, the distinction between mixtures and pure substances lies at the root of the historical separation of organic and polymer chemistry. From the perspective of oligomer chemistry, it is a worthwhile exercise to briefly examine how this separation came about. In 1907, at a time when many chemists believed that high molecular weight organic molecules simply did not exist, Emil Fischer (1907) succeeded in preparing an oligopeptide chain of eighteen amino acid residues. Fischer wrote, “In studying substances of high molecular weight, molecular physics should restrict itself to synthetic products of known structure. I shall therefore continue experiments on the build-up of giant molecules” (Morawetz, 1985). Fischer apparently held the belief that, just as physical chemistry is con-



**Figure 1-1.** Plot showing the variation of melting point and lamellar thickness as a function of oligomer chain length for acetoxy capped formaldehyde oligomers (Staudinger et al., 1927). The melting point of the oligomer increases smoothly, asymptotically approaching the value of the high polymer (oligomer length =  $n$ ).

cerned with the details of atomic and molecular structure, synthetic organic chemistry should strive to clarify the limits of molecular size.

It was 1920 when Staudinger proposed the hypothesis of *hochmolekulare Verbindungen*, and within the short span of seven years he gathered irrefutable evidence for the chain structure of polymers. Some of his strongest evidence came from a homologous series of acetoxy end-capped oligomers of formaldehyde (Staudinger et al., 1927). These oligomers were prepared as a mixture by oligomerization and painstakingly separated into discrete members by classical methods. Using these substances, Staudinger showed that the changes in the physical properties (e.g., solubility, melting point) versus the chain length smoothly extrapolated to the value of the polymer. For example, Fig. 1-1 shows a plot of melting point versus oligomer length, where it can be seen that the melting point smoothly increases and asymptotically approaches that of the high polymer. Powder X-ray diffrac-

tion data showed that the lamellar spacing of the crystalline oligomers increased linearly with chain length, although this behavior did not continue to hold to the high polymer limit because of chain folding.

Soon after these results were published, the practical and industrial significance of polymeric materials became apparent, and synthetic efforts to make discrete, high molecular weight products of known structure lost appeal. Industrial polymer chemist Wallace Carothers set the agenda for the next 60 years. In a *Chemical Reviews* article titled "Polymerization" published in 1931, Carothers wrote: "The step-by-step synthesis of long molecular chains containing a repeating unit is illustrated by Fischer's synthesis of polypeptides. Reactions of polymerization, however, lead to the formation of polymeric chains in a single operation. . . . It is true that synthetic linear high polymers are invariably mixtures whose molecules are chains of slightly differing lengths. . . . Nevertheless, it must be admitted that a molecule does not lose any of its definiteness as an entity (because) it cannot be completely separated from other similar but slightly different molecules."

Thus began the polymer industry, leaving mostly only those chemists interested in biopolymers to study discrete, high molecular weight substances. Fortunately, the situation changed dramatically in 1985 when Don Tomalia and George Newkome disclosed their invention of dendritic macromolecules (Tomalia et al., 1985; Newkome et al., 1985). The construction of dendrimers represents a modern-day example of repetitive constructions for preparing discrete oligomeric substances. It might be said that this work helped to stimulate interest in well-defined large molecules and thus paved the road for a return to Fischer's vision of high molecular weight "products of known structure".

### 1.3 Overview of Synthetic Strategies

As shown in Fig. 1-2, there are three general strategies that have been used in the repetitive construction of oligomers. The reactions involved in the repetitive cycles include various combinations of coupling and deprotection steps. In Fig. 1-2, the coupling steps involve bond formation between reactive groups represented as A and B, while the deprotection steps convert the protected functionalities (represented as  $A_p$  or  $B_p$ ) to their reactive forms. Obviously, the most important criterion of any successful repetitive method is that all of the reactions be of extremely high fidelity (i.e., very high yields independent of monomer and chain length).

Figure 1-2a shows a simple repetitive sequence in which a single monomer is added during each cycle. This particular scheme also illustrates the use of a solid support, as pioneered by Merrifield (1963) for oligopeptides and now commonly used for a wide range of synthetic applications (Fruchtel and Jung, 1996; Thompson and Ellman, 1996). In the case of solid phase synthesis, the oligomerization process begins by coupling a “start monomer” onto the polymer resin, as indicated in Fig. 1-2a. For solution phase synthesis, on the other hand, an inert end group (EG) would simply be introduced at the start of the synthesis rather than attaching the monomer to the polymer support. Figure 1-3 shows a plot of oligomer length versus the number of repetitions. It can be seen that a disadvantage of the simple repetitive sequence is the slow rate of chain growth relative to the other oligomerization methods described below.

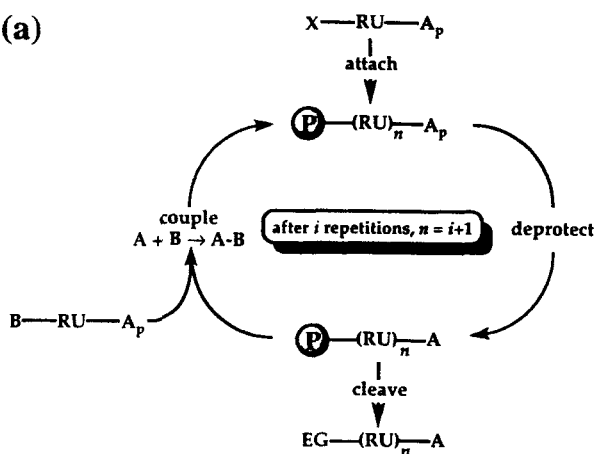
The use of a polymer support for oligomer synthesis offers several advantages, including the ease of workup and greatly simplified purification. Solid phase methods al-

so facilitate the use of excess monomer in high concentrations to drive bimolecular coupling processes to completion without the complication of a difficult monomer/oligomer separation once the reaction is finished. Moreover, solid phase methods can sometimes capitalize on the site-isolation principle (Leznoff, 1978), which allows readily available symmetrical difunctional monomers to be used for oligomer growth. Another attractive feature of the solid phase methods is that they are easily adapted to combinatorial and automated procedures, enabling the simultaneous preparation of as many as  $10^6$  different peptide sequences (Jung and Beck-Sickinger, 1992). When the combinatorial approach is used in conjunction with an effective screening protocol, a wide variety of substrates can be tested for a desired property or activity. Finally, it should be noted that solid phase methods are not restricted to oligomerizations in which growth involves single monomer addition; they can be applied to the orthogonal and the divergent/convergent methods described below.

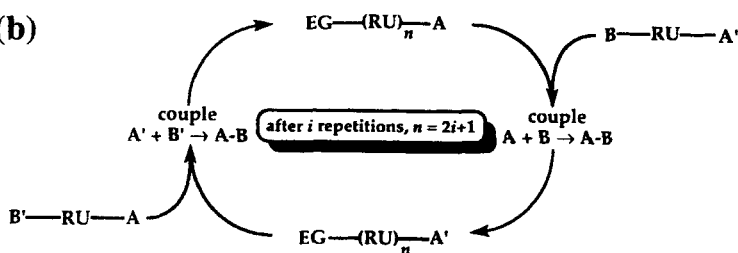
Figure 1-2b shows an orthogonal coupling strategy for repetitive oligomer synthesis (the reactive functional groups are denoted A, B, A', and B'). The main advantage of the orthogonal approach is that each synthetic step in the repetitive cycle productively contributes to the chain growth. This is achieved with a pair of complementary and selective coupling reactions, such that group A only reacts with B while A' only reacts with B'. Because of the orthogonality of these reactions, no protecting groups or deprotection steps are required. Thus with each repetitive cycle, two monomer units are added. The rate of growth is twice as fast as in simple monomer addition, as seen in Fig. 1-3.

Figure 1-2c shows how oligomers are prepared by the repetitive divergent/conver-

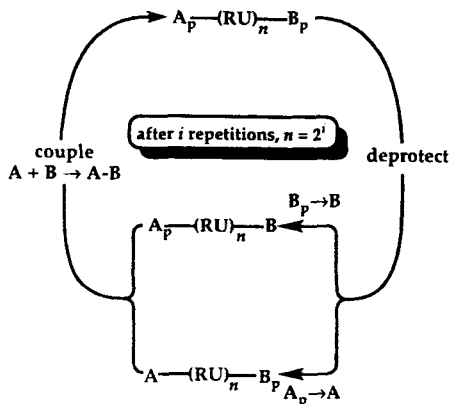
(a)



(b)

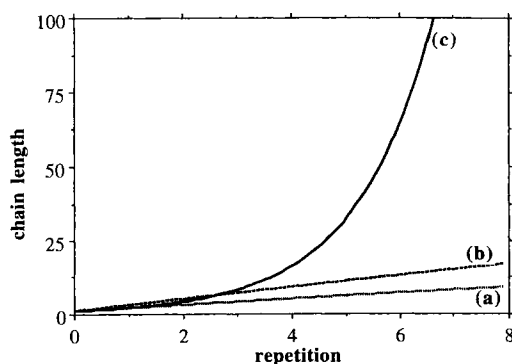


(c)



**Figure 1-2.** The three generalized strategies for repetitive oligomer synthesis (RU represents the oligomer's repeat unit; A, B, A', and B' are reactive functional groups used to join new segments to the growing oligomer;  $A_p$  and  $B_p$  are the protected forms of A and B; EG is the end-group functionality).

(a) Simple repetitive oligomer synthesis on a solid support in which a single monomer ( $B-RU-A_p$ ) is added with each repetition. (b) Orthogonal repetitive synthesis with two selective coupling steps per repetition. (c) Molecular doubling strategy by the divergent/convergent process in which growth takes place at both ends allowing for a non-linear dependence of the growth rate with respect to the number of repetitions.



**Figure 1-3.** Oligomer length (i.e., number of monomers per chain) vs. the number of repetitions for the three strategies shown in Fig. 1-2. The slope of the line represents the rate of oligomer growth. For the divergent/convergent growth strategy (c), it can be seen that there is an acceleration in the growth rate as the chain length increases. (a) Single monomer growth. (b) Orthogonal growth. (c) Repetitive divergent/convergent growth.

gent scheme. In this case, growing oligomeric fragments are coupled together (Wang, 1973) to greatly accelerate the oligomerization rate (Fig. 1-3), without sacrificing chemical integrity. The method begins by selectively deprotecting each of the two ends of the diprotected monomer  $A_pB_p$  yielding the two monoprotected intermediates  $A_pB$  and  $AB_p$ . These are then coupled to give the dimer  $A_pBAB_p$ , protected in the same way as the original monomer (one repetition now complete). The process can be repeated  $i$  times to give a sequence of length  $2^i$ , with each cycle requiring a total of three synthetic steps. Figure 1-3 shows how the rate of oligomer growth accelerates during the oligomerization process. Clearly the divergent/convergent method offers a faster way to construct long oligomers. Sequences of length other than  $2^i$ , as well as sequences having a particular arrangement of comonomers, can be realized by merging parallel repetitive cycles. For example, a hexamer sequence is realized by combining tetramer and dimer sequences. The use of

these various methods will be made clear in the following sections which survey repetitive chemistry used in oligomer syntheses.

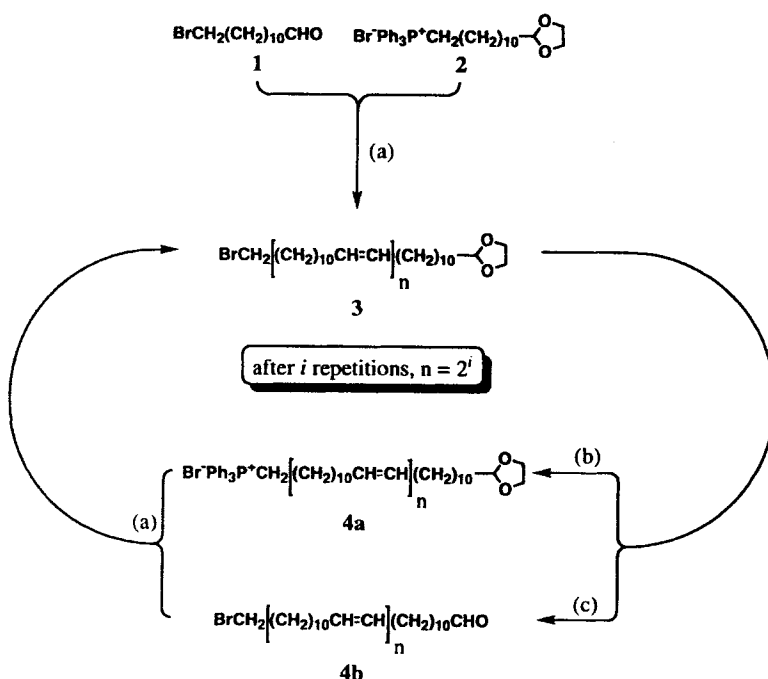
## 1.4 Repetitive Oligomer Syntheses

In the following section, specific examples from recent literature illustrating the three oligomerization methods are presented. These examples are categorized according to the type of bond-forming reaction used in the oligomerization process. In the first section, the oligomerizations are all based on carbon-carbon bond forming reactions. The second section describes heteroatom linkages used in chain growth.

### 1.4.1 Oligomerizations Based on Carbon-Carbon Bond Constructions

The synthesis of long chain linear alkanes by controlled oligomer growth has been achieved using an exponential growth method that is shown in Scheme 1-1 (Whiting et al., 1987, 1996). The synthesis involved three reactions for each repetitive cycle. Starting compounds **1** and **2** were readily prepared in large quantities from commercially available materials. A Wittig reaction between **1** and **2** provided monomer **3** ( $n=1$ ). This monomer was the starting point for subsequent growth of longer alkyl chains. The terminal aldehyde and phosphonium salt were masked as the ethylene acetal and alkyl bromide, respectively. Further growth was performed by coupling monoprotected oligomers. In particular, a portion of the material was converted to aldehyde **4b** by acid-catalyzed acetal hydrolysis, while the remainder was transformed to the phosphonium salt **4a** by reaction with triphenylphosphine. A Wittig reaction be-

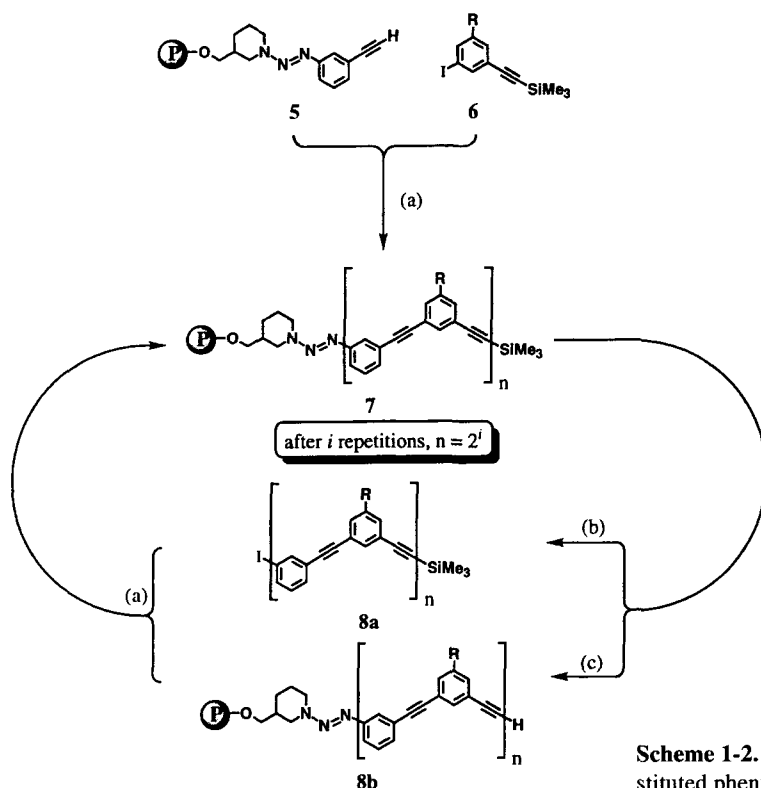




**Scheme 1-1.** Repetitive synthesis of long chain alkanes using a divergent/convergent method (Whiting et al., 1987, 1996). Reagents: (a) lithium diisopropylamide, THF,  $-10^\circ\text{C}$ ; (b) triphenylphosphine,  $103^\circ\text{C}$ ; (c) 25% *p*-toluenesulfonic acid, water: sulfolane (1:1), silica gel.

tween **4a** and **4b** resulted in the formation of **3** ( $n=2$ ). Upon reaching the desired oligomer length ( $n$ ), oligomer **4b** was "capped" with shorter chain phosphonium salts via the Wittig reaction. The halides of these oligomers were then removed with lithium triethylborohydride and the double bonds reduced by hydrogenation, giving the desired alkanes. The longest alkane synthesized using this method was  $\text{C}_{390}\text{H}_{782}$ . Although this method does allow for discrete, high molecular weight alkanes to be obtained, there are some drawbacks. The major problem is that long reaction times are necessary for the formation of phosphonium salts (**3**  $\rightarrow$  **4a**). In some cases up to 28 days were required for complete reaction. This resulted in the formation of side products, with removal of the ethylene acetal being the major impurity. It was possible to determine the purity of the intermediates by  $^1\text{H}$  NMR and HPLC. HPLC analysis required transformation of aldehydes **4b** to the corresponding DNP derivative.

Several different repetitive methods for synthesizing sequence-specific phenylene ethynylene oligomers have recently been reported. One of these was described by Moore and coworkers involving the use of an insoluble polymer support to synthesize meta-connected oligomers (Moore et al., 1994). As shown in Scheme 1-2, the terminal acetylene (Earborn and Walton, 1965) and aryl iodide moieties were orthogonally masked as the (trimethylsilyl)-acetylene and 1-aryl-3,3-dialkyltriazene groups (Moore et al., 1991; Wu and Moore, 1994) respectively. Sonogashira coupling (Sonogashira et al., 1975) between polymer-bound terminal acetylene **5** and aryl halide **6** afforded the polymer-bound dimer **7**, which contains the orthogonal protecting groups suitable for subsequent oligomer growth. Utilizing a fragment condensation approach (Wang, 1973), a portion of the polymer-supported sequence **7** was liberated by treatment with methyl iodide to afford aryl iodide **8a**. The remainder of the supported

R = *tert*-butyl

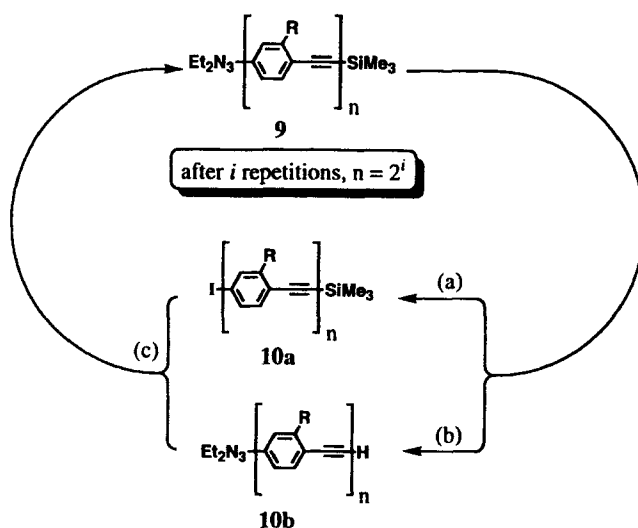
repetition (i)	change in n	Yield (%)
1	1 → 2	65
2	2 → 4	50
3	4 → 8	80

**Scheme 1-2.** Repetitive synthesis of *m*-substituted phenylene ethynylene oligomers using a divergent/convergent method on a solid support (Moore et al., 1994, 1996). Reagents: (a) bis(dibenzylideneacetone)palladium(0), cuprous iodide, triphenylphosphine, triethylamine, DMF, 65 °C, 24 h; (b) methyl iodide, 110 °C, 6 h; (c) potassium hydroxide, THF, MeOH, 75 °C, 1 h.

sequence was then converted to the terminal acetylene **8b**. Coupling of **8a** and **8b** afforded **7** ( $n=2$ ). Each individual step of the reaction was monitored by infrared analysis of the polymer-bound oligomer. The overall process doubled the chain length during each repetition allowing for the synthesis of **7** ( $n=8$ ), with 50% yield overall. This method has several advantages over the solution phase methods (Moore and Zhang, 1992), with the major one being the reduced time required for purification of the products. Synthesis of **7** ( $n=16$ ) resulted in the formation of 95% desired product, with the major impurity being **8b** ( $n=8$ ). This was

attributed to the growing oligomers no longer being accessible on the polymer support due to the high polymer loading. It has since been shown that it is possible to use a direct triazene linkage to the solid support and that a wide variety of monomers **6** can be used to synthesize sequence-specific oligomers (Moore et al., 1996).

Related procedures have been used by Tour et al. (1997) to synthesize para-connected phenylene ethynylene oligomers, as shown in Scheme 1-3. The terminal acetylene and aryl halide moieties were again orthogonally masked as the (trimethylsilyl)-acetylene and 1-aryl-3,3-dialkyltriazene



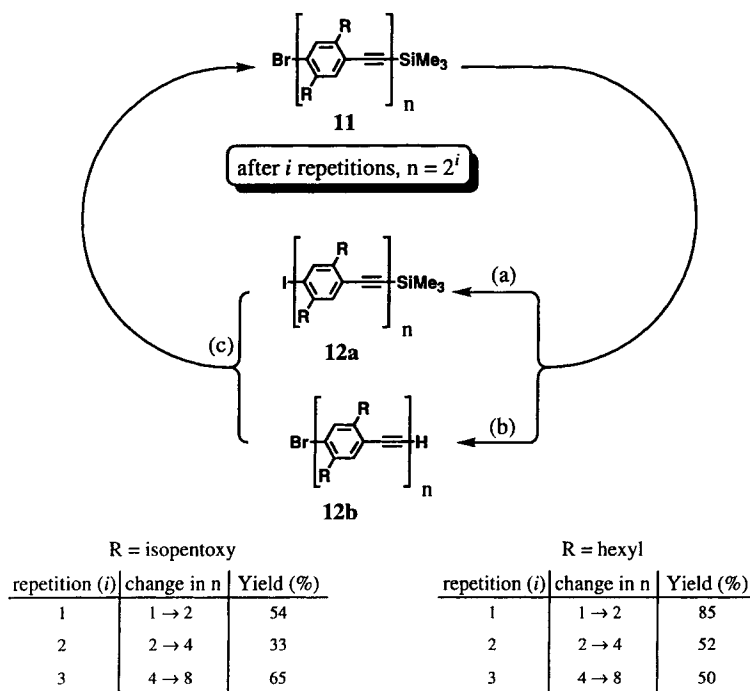
R = ethyl			R = 3-ethylheptyl			R = dodecyl		
repetition (i)	change in n	Yield (%)	repetition (i)	change in n	Yield (%)	repetition (i)	change in n	Yield (%)
1	1 → 2	89	1	1 → 2	72	1	1 → 2	80
2	2 → 4	89	2	2 → 4	43	2	2 → 4	83
			3	4 → 8	70	3	4 → 8	44
			4	8 → 16	26	4	8 → 16	81

**Scheme 1-3.** Repetitive synthesis of *p*-linked phenylene ethynylene oligomers using a divergent/convergent method (Tour et al., 1997). Reagents: (a) methyl iodide; (b) potassium carbonate, MeOH, or tetrabutylammonium fluoride, THF; (c) bis(dibenzylideneacetone) palladium(0), cuprous iodide, triphenylphosphine, diisopropylamine, THF, rt.

groups, respectively. Removal of the trimethylsilyl group of **9** gave terminal acetylene **10b**. Conversion of triazene to aryl iodide **10a** followed by subsequent coupling with **10b** afforded compound **9** ( $n=2$ ). Using this growth scheme, several different homooligomers with different R groups were synthesized. It was found to be necessary to use long, branched alkyl chains to ensure solubility in the longer length oligomers **9** ( $n=8$ ). Using monomer **9** ( $n=1$ ), functionalized with R groups of 3-ethylheptyl or dodecyl, it was possible to synthesize oligomer **9** ( $n=16$ ), which is 128 Å (12.8 nm) in its linear extended conformation. The synthesis of oligomer **9**, where R = dodecyl, was also achieved by utilizing solid phase methodology (not shown). Each reaction

step was monitored by infrared analysis and gel-phase  $^{13}\text{C}$  NMR. The solid phase method allowed for the synthesis of **10a** ( $n=16$ ), with an overall yield of 79%. This corresponds to an average yield of 92% over the three steps (deprotection, coupling, and cleavage). This result is an enormous improvement over the solution phase synthesis of the same oligomer. In the solution phase synthesis only a 24% yield was obtained for the desired oligomer.

An alternative approach to para-connected phenylene ethynylene oligomers has recently been described by Godt and Ziener (1997). As shown in Scheme 1-4, the terminal acetylene and aryl iodide are masked as the (trimethylsilyl)-acetylene and aryl bromide, respectively. Removal of the trimeth-



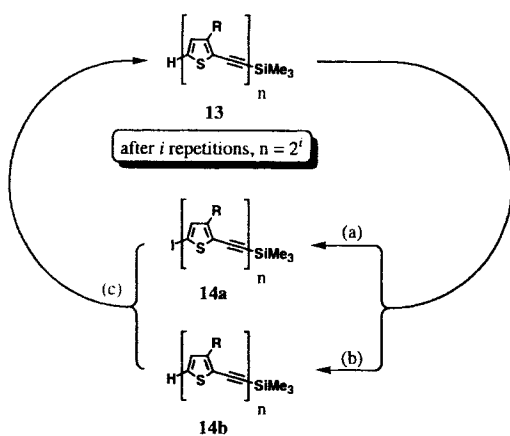
**Scheme 1-4.** Repetitive synthesis of *p*-linked phenylene ethynylene oligomers using a divergent/convergent method (Godt and Ziener, 1997). Reagents: (a) (1) *n*-butyl lithium, (2) 1,2-diiodoethane; (b) sodium hydroxide, H<sub>2</sub>O, THF, MeOH; (c) dichlorobis(triphenylphosphine) palladium (II), cuprous iodide, diethylamine, rt.

ylsilyl group of **11** results in terminal acetylene **12b**. Conversion of the aryl bromide of **11** to the aryl iodide **12a** was achieved via metal-halogen exchange. The key step in the growth sequence is the chemoselective palladium-catalyzed coupling of the aryl iodide **12a** and the terminal acetylene **12b**, resulting in the formation of **11** ( $n=2$ ). The authors reported that no reaction was observed between the acetylene and the bromide of **12b**. Using this three-step divergent/convergent growth method, it was possible to synthesize **11** ( $n=8$ ), with side groups of R=isopentoxy and R=hexyl. The overall yields of oligomers **11** ( $n=8$ ) are 10% (R=isopentoxy) and 22% (R=hexyl). The yields of the coupling reactions are lower for the longer length oligomers. This was due to a small amount of homocoupling (5–10% as determined by <sup>1</sup>H NMR) which was observed between two molecules of acetylene **12b**. The main advantage that this method offers over those previously de-

scribed is that it does not involve the use of volatile carcinogenic methyl iodide for the formation of the aryl iodide.

The repetitive, controlled growth of oligothiophenes is shown in Scheme 1-5 (Tour and Pearson, 1997). Removal of the trimethylsilyl group of **13** gave terminal acetylene **14b**. Introduction of the iodide group to the growing oligomers was achieved by the regioselective addition of iodine to the 5-position of the terminal thiophene moiety, resulting in **14a**. A palladium-catalyzed cross coupling between **14a** and **14b** provided **13** ( $n=2$ ). Using this repetitive divergent/convergent approach, **13** ( $n=16$ ) was synthesized with a 13% overall yield. As the oligomer lengths became longer, the reaction yields decreased significantly, due to the oxidative instability of **14b** ( $n=4$  and  $n=8$ ).

The synthesis of rigid oligophenylenes has been performed by Schlüter et al. (1996) using the repetitive divergent/convergent growth method that is outlined in Scheme

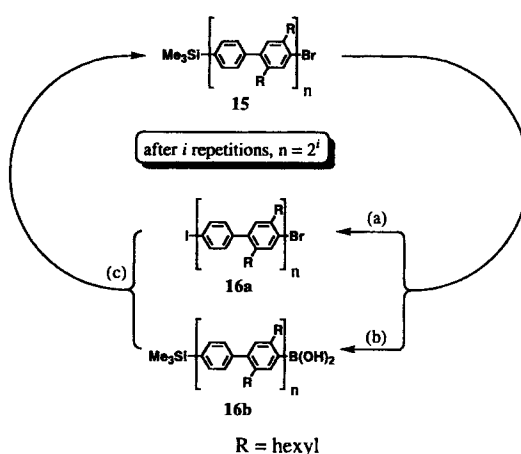


R = ethyl

repetition (i)	change in n	Yield (%)
1	1 → 2	84
2	2 → 4	73
3	4 → 8	67
4	8 → 16	32

**Scheme 1-5.** Repetitive synthesis of thiophene ethynylene oligomers using a divergent/convergent method (Tour and Pearson, 1997). Reagents: (a) lithium diisopropylamide,  $\text{Et}_2\text{O}$ ,  $-78 \rightarrow 0^\circ\text{C}$  then iodine,  $-78^\circ\text{C}$ ; (b) potassium carbonate,  $\text{MeOH}$ , rt; (c) dichlorobis(triphenylphosphine)palladium (II), cuprous iodide, diisopropylamine, THF, rt.

1-6. The repetitive process involved masking an aryl iodide as a trimethylsilyl group and conversion of an aryl bromide to the corresponding boronic acid. Oligomer growth involved conversion of **15** to the iodo-bromo oligophenylene **16a** and the conversion of **15** to the corresponding boronic acid **16b**. The key step in the synthesis is the selective Suzuki coupling of iodide **16a** and the boronic acid **16b**, resulting in the formation of **15** ( $n=2$ ). In all cases the conversion of **15** to **16a** and **16b** resulted in high reaction yields ( $>82\%$ ). Suzuki couplings of longer length oligomers gave reduced yields. Nonetheless, this methodology did allow for the synthesis of the longest monodisperse oligophenylene rod that has been reported to date (**15**,  $n=8$ ).

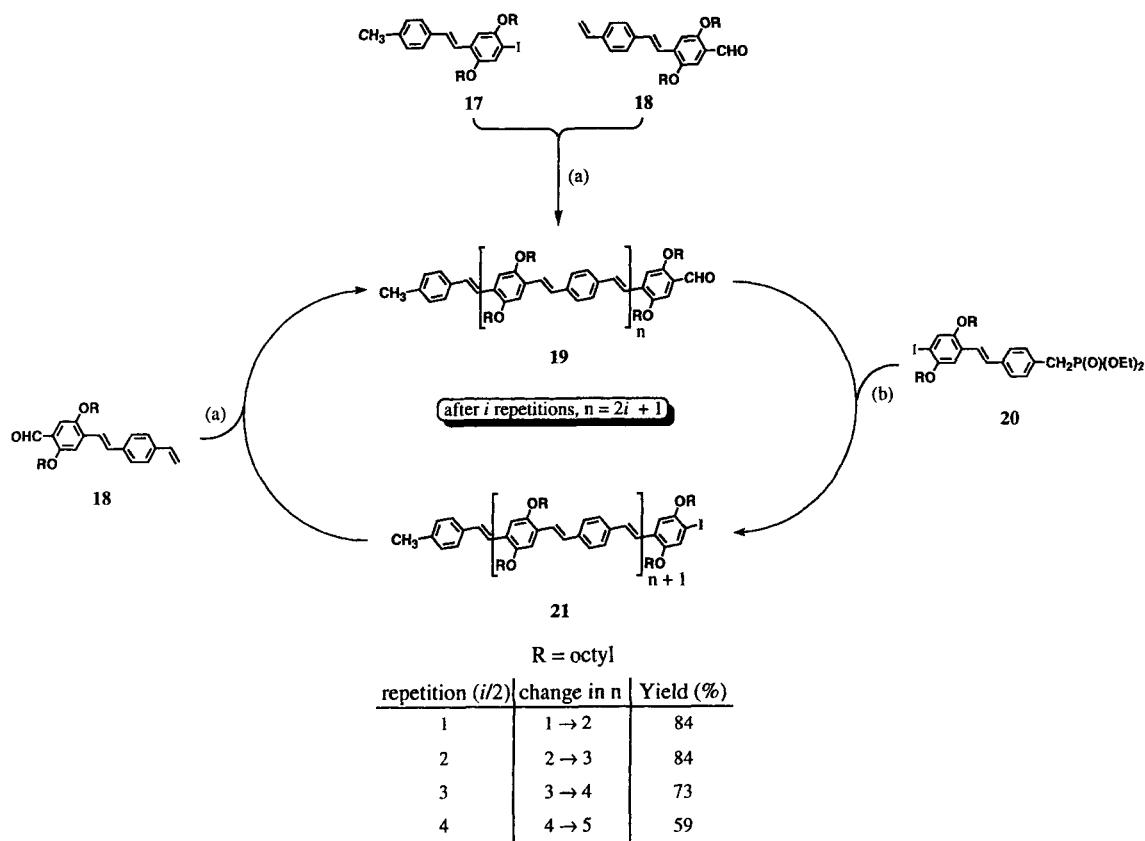


R = hexyl

repetition (i)	change in n	Yield (%)
1	1 → 2	61
2	2 → 4	27

**Scheme 1-6.** Repetitive synthesis of oligophenylenes using a divergent/convergent method (Schlüter et al., 1996). Reagents: (a) iodine monochloride,  $\text{CCl}_4$ ,  $0^\circ\text{C}$ , (b) (1) *n*-butyl lithium,  $\text{Et}_2\text{O}$ ,  $-78^\circ\text{C}$ , (2) triisopropyl borate; (c) tetrakis(triphenylphosphine) palladium(0), sodium carbonate, toluene,  $112^\circ\text{C}$ , 48 h.

An orthogonal approach to the synthesis of phenylenevinylene oligomers has been reported by Yu and coworkers (Scheme 1-7) (Yu et al., 1997). This method offers the advantage that no protecting group is required and each synthetic transformation contributes to the oligomer group. The concept is related to Zimmerman's orthogonal convergent dendrimer synthesis (Zimmermann and Zeng, 1996). To control the oligomer growth, compound **17** was used to cap one end of monomer **18**. The two reactions used for the orthogonal growth are a Heck reaction between a terminal alkene and aryl iodide, and a Horner-Wadsworth-Emmons reaction between an aldehyde and a phosphonate. Coupling of the first monomer pair was performed by a Horner-Wadsworth-Emmons reaction between aldehyde **19** and phosphonate **20**. The next

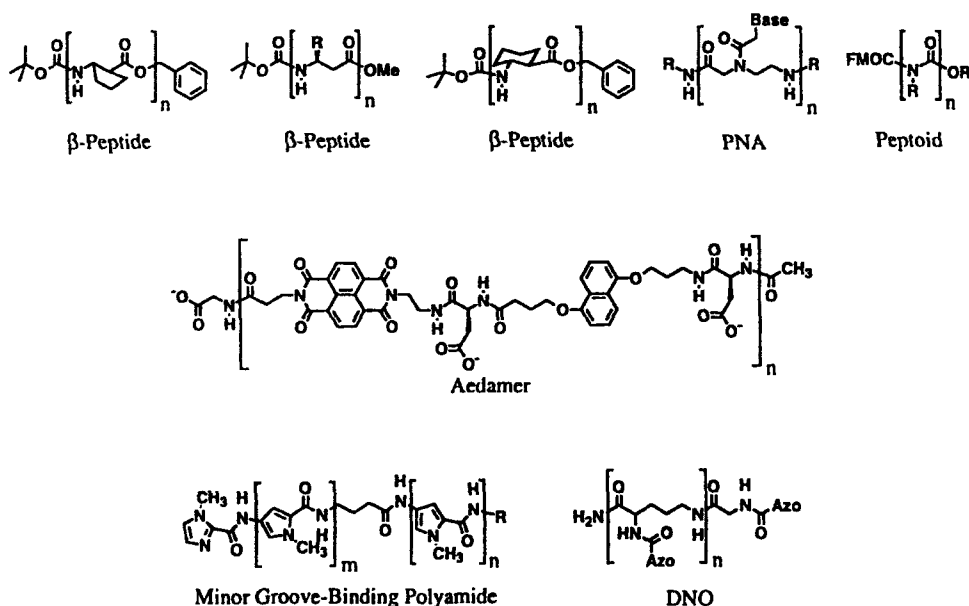


**Scheme 1-7.** Repetitive orthogonal synthesis of phenylenevinylene oligomers (Yu et al., 1997). Reagents: (a) palladium(II) acetate, tri-*o*-tolylphosphine, tributylamine, DMF; (b) sodium hydride, dimethoxyethane.

monomer was added using the Heck reaction between alkene **18** and aryl iodide **21**. The desired oligomers contained trans-substituted double bonds. However, both the Heck and Horner-Wadsworth-Emmons reactions did result in the formation of the cis product. In the case of the Heck reaction, <4% of the cis olefin was observed, while ~5% of the cis olefin was seen in the Horner-Wadsworth-Emmons reaction, as determined by NMR spectroscopy. The minor cis-double bond impurities were removed by silica gel column chromatography. This orthogonal synthesis allowed for oligomer **19** ( $n=5$ ), to be synthesized with an overall 30% yield.

#### 1.4.2 Oligomerizations Based on Heteroatom Bond Constructions

As a result of their biological significance, oligopeptides are arguably the most widely studied heteroatom-containing oligomers. The repetitive methods used to prepare these oligomers have been thoroughly studied and reviewed (Barany and Merrifield, 1979; Bayer, 1991); therefore, the synthetic chemistry used to construct oligopeptides will not be considered in further detail here. Many researchers have capitalized on the well-established oligopeptide methodology to prepare interesting new nonbiological oligopeptides. Figure 1-4 shows



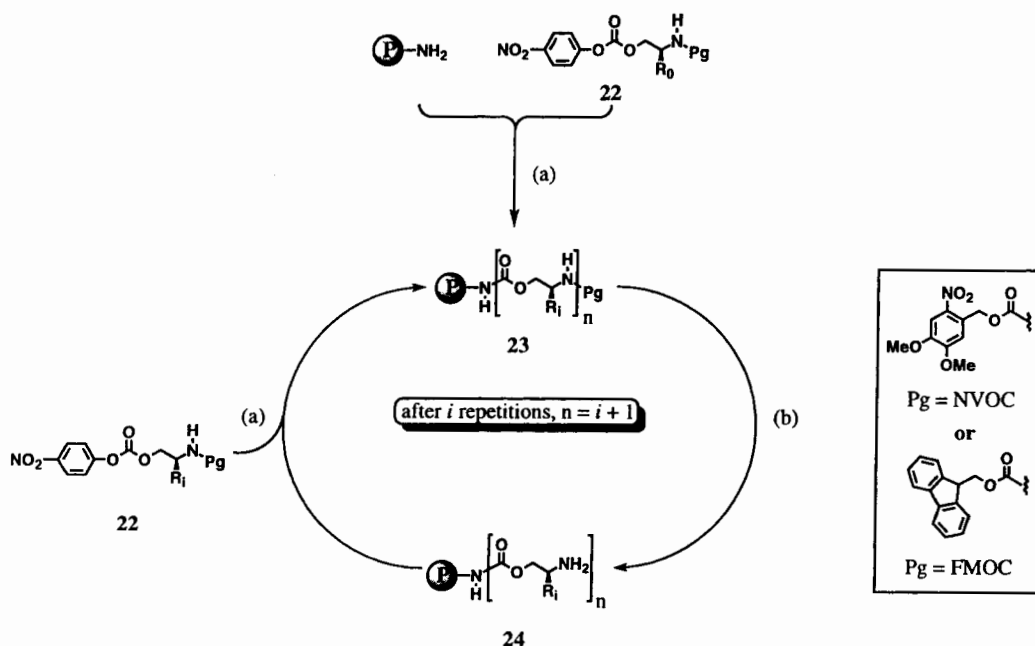
**Figure 1-4.** Recent examples of nonbiological oligoamides prepared by repetitive syntheses. (Base refers to a nucleobase and Azo refers to an azobenzene chromophore.) References to the original literature are as follows:  $\beta$ -peptides (Gellmann et al., 1996; Seebach et al., 1996a, b), polyamide nucleic acids (PNAs) (Nielsen and Haaime, 1997; Duchalm and Nielsen, 1997), peptoids (Zuckermann et al., 1992), aedamers (Lokey and Iverson, 1995), minor groove-binding polyamides (Trauger et al., 1996), diamino acid- $N^\alpha$ -substituted oligopeptides (DNOs) (Berg et al., 1996).

representative examples that have recently been studied. Several of these, such as the  $\beta$ -peptides (Koert, 1997), will be discussed in Sec. 1.5 of this Chapter. Here the repetitive chemistry used in the construction of other heteroatom-containing oligomers will be provided.

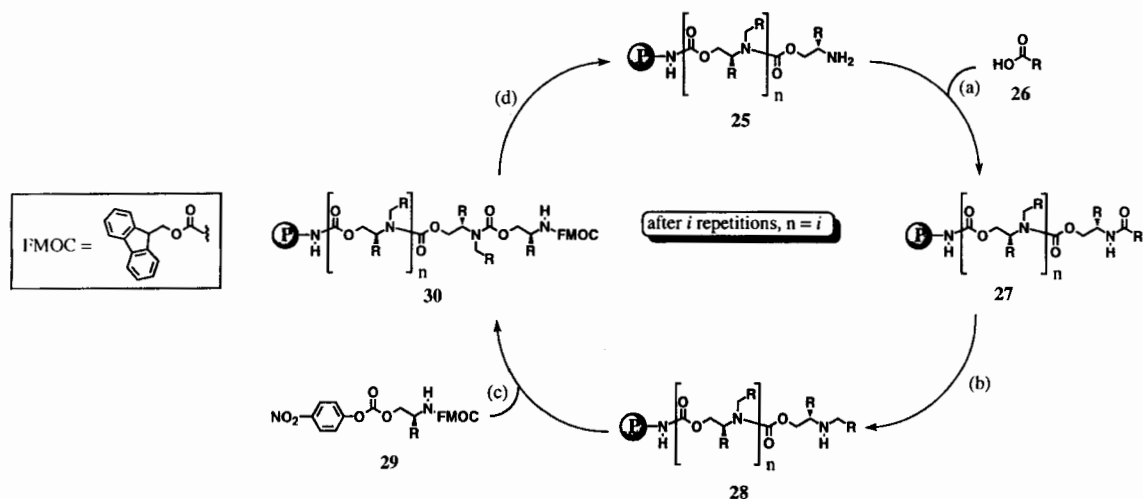
The synthesis of carbamate oligomers is shown in Scheme 1-8 (Schultz et al., 1993). The monomers used for oligomer growth **22** can be synthesized in two steps from commercially available, optically active amino alcohols. Over twenty oligocarbamate monomers have been synthesized, which allows for a large amount of diversity in the growing oligomer chains (Schultz et al., 1995). Each addition of a monomer required two steps. The reaction of Fmoc-protected monomer **22** with polymer-bound amine gave carbamate **23** ( $n=1$ ). Subsequent

growth of the oligomer involved removal of the protecting group with piperidine to give amine **24**. This amine was then reacted with another monomer to give dimer **23** ( $n=2$ ). This two-step cycle gave an overall yield of >99% reaction efficiency for each round of synthesis. In order to create libraries of the oligocarbamates, a light-directed parallel synthesis method was carried out on glass substrates. In this case, the light removable protecting group (NVOC) was used for monomer **22** (Schultz et al., 1993). Reaction yields were still very high (>90%) and allowed for the synthesis of 256 different oligocarbamates **23** ( $n=8$ ).

The synthesis of  $n$ -alkylcarbamate oligomers has also been developed, as shown in Scheme 1-9 (Schultz et al., 1996a). Four steps are required for the addition of each monomer unit. Polymer-bound amine **25**

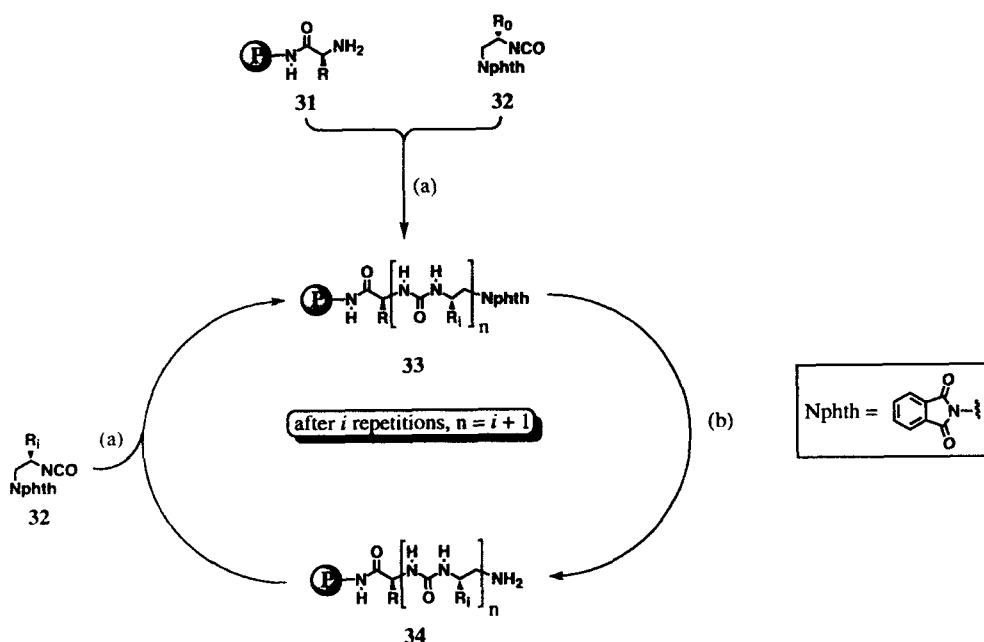


**Scheme 1-8.** Repetitive solid phase synthesis of carbamate oligomers (Schultz et al., 1993). Reagents: (a) hydroxybenzotriazole, diisopropylethylamine, NMP, 25 °C, 4 h; (b) piperidine : NMP (2 : 8) (Pg = Fmoc) or 365 nm light (Pg = NVOC).



**Scheme 1-9.** Repetitive solid phase synthesis of  $n$ -alkylcarbamate oligomers (Schultz et al., 1996 a). Reagents: (a) hydroxybenzotriazole, HBTU, diisopropylethylamine, DMF; rt., 1 h; (b) (1) borane, THF, 50 °C, 1 h, (2) DBU, NMP:MeOH (9 : 1), rt.; (c) hydroxybenzotriazole, diisopropylethylamine, THF, 50 °C; (d) piperidine : NMP (2 : 8).



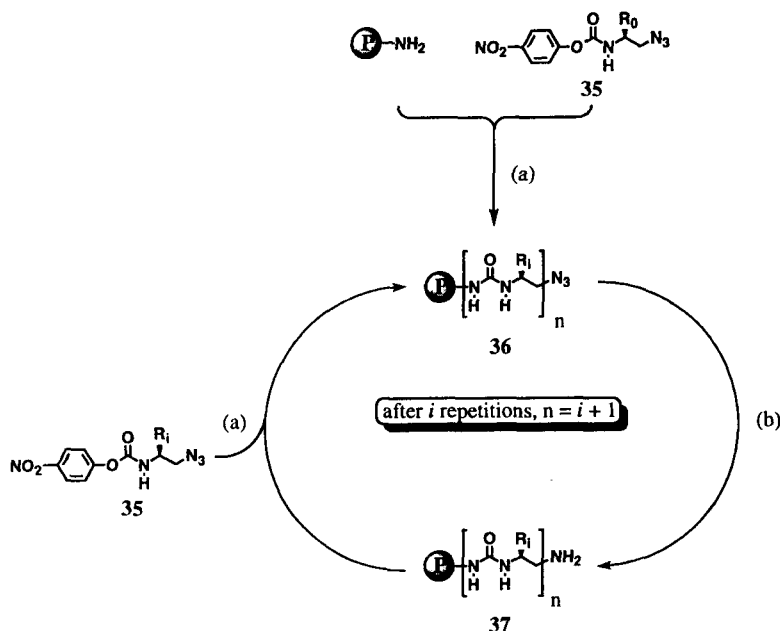


**Scheme 1-10.** Repetitive solid phase synthesis of oligoureases (Burgess et al., 1995, 1997). Reagents: (a)  $\text{CH}_2\text{Cl}_2$ , rt., 11 h; (b) 60% hydrazine in DMF, 1–3 h.

( $n=0$ ) was used for the synthesis of the carbamate oligomers. The first step of the repetitive cycle was acylation of the amine with a carboxylic acid **26**. Benzoic, acetic, and 2-methylpropionic acid were utilized for this acylation. The second step involved selective reduction of the amide linkage in **27** with borane, yielding  $n$ -alkyl amine **28**. Using these conditions, the amide linkage was selectively reduced in the presence of the carbamate linkage. The third step of the cycle was the reaction of **28** with protected monomer **29**. This monomer is synthesized in two steps from commercially available amino alcohols. Deprotection of **30** to give **25** ( $n=1$ ) brings the repetitive cycle back to the beginning. Using this methodology, four pentamers were synthesized in overall yields of 70–90%. A variety of side chains on the oligomer backbone were utilized, including amino, guanidine, and hydroxy.

Several methods have been developed for the synthesis of oligoureases. One of these is

the sequence developed by Burgess and co-workers shown in Scheme 1-10 (Burgess et al., 1995, 1997). Two steps were required for the addition of each monomer unit. Monomer **32** was prepared in five steps from protected amino acids. In this sequence the urea linkage was formed via the in situ activation of monomer **32** as an isocyanate. The amine was protected as a naphthalimide. Reaction of the polymer-bound amine **31** and isocyanate **32** resulted in the formation of the first urea linkage giving **33** ( $n=1$ ). Subsequent growth was accomplished by removal of the naphthalimide protecting group on **33** by treatment with hydrazine to give free amine **34**. This amine was then reacted with the next monomer **32** to give **33** ( $n=2$ ). This process was used to synthesize four different oligomers of **33** ( $n=4$ ). The overall yields were fairly low, ranging between 9 and 46%. The major problem was the removal of the naphthalimide protecting group, which required fair-



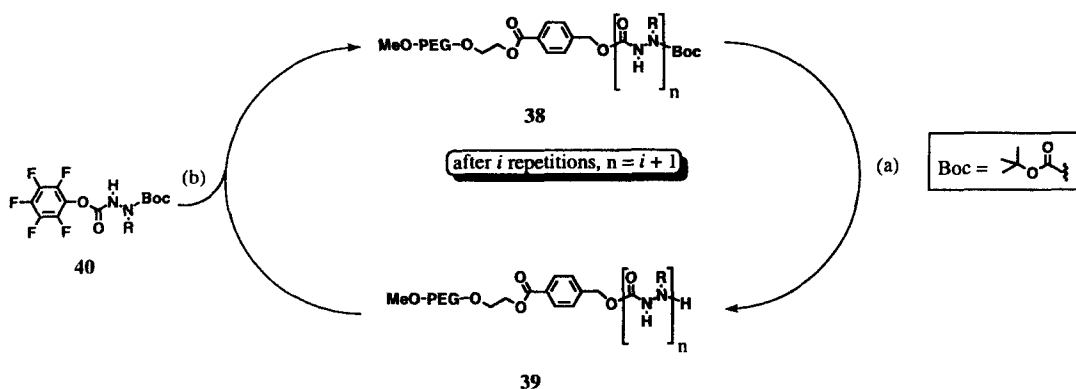
**Scheme 1-11.** Repetitive solid phase synthesis of oligoureases (Schultz et al., 1996 b). Reagents: (a) diisopropylethylamine,  $\text{CH}_2\text{Cl}_2$ , rt., 4 h; (b) tin (II) chloride, triethylamine, thiophenol, THF, rt., <2 h.

ly long reaction times and did not give high yields.

In an alternative approach to the synthesis of oligoureases, Schultz and coworkers have used the process outlined in Scheme 1-11 (Schultz et al., 1996 b). The process required the same number of steps, but it resulted in a much higher yield of the desired oligomers compared to the method developed by Burgess. Monomer **35** could be prepared from commercially available amino alcohols in four steps to give a high yield (50–80%). In this sequence the carbonyl group of the monomer was activated with *p*-nitrophenol and the amine was masked as the azide. The reaction between the polymer-bound amine and monomer **35** formed the first urea linkage giving **36** ( $n=1$ ). Reduction of the azide **36** with tin chloride gave free amine **37**, with a quantitative yield and short reaction times (<2 h). Reaction of amine **37** with the next monomer **35** produced **36** ( $n=2$ ). This methodology was

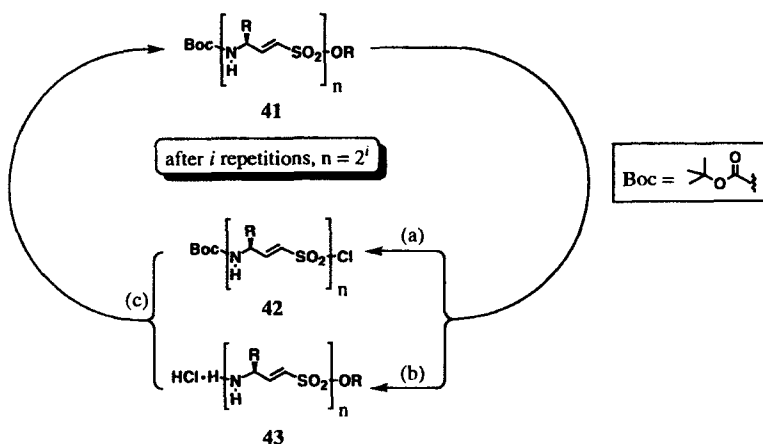
used to synthesize four oligomers, up to  $n=4$ , with an overall purified yield of 54–76%. A related series of cyclic urea oligomers has also been reported by Schultz (Schultz et al., 1996 c). Although this work has not yet been applied to solid phase chemistry, it was possible to synthesize a cyclic urea trimer in moderate yields.

The synthesis of azatide oligomers is shown in Scheme 1-12. Both a solution and liquid phase synthesis of these oligomers have been reported (Janda and Han, 1996). The solution phase methodology only allowed for the synthesis of dimers. However, by utilizing a liquid phase “solid support”, it was possible to synthesize longer oligomers. Monomer **40** was synthesized via reaction with hydrazine and an alkyl halide followed by BOC protection of the hydrazide and in situ activation with bis(pentafluoro) carbonate. The addition of each monomer unit required two steps. The BOC-protecting group on the polymer-bound aza-



MeO-PEG = poly(ethylene glycol) monomethyl ether

**Scheme 1-12.** Repetitive solution phase synthesis of azatide oligomers (Janda and Han, 1996). Reagents: (a) trifluoroacetic acid,  $\text{CH}_2\text{Cl}_2$ , diisopropylethylamine, 30 min; (b) *N,N*-dimethylaminopyridine,  $\text{CH}_2\text{Cl}_2$ , rt., 30 min.



**Scheme 1-13.** Repetitive solution phase synthesis of vinylous sulfonamide oligomers (Gennari et al., 1994). Reagents: (a) (1) tetrabutylammonium iodide, acetone,  $56^\circ\text{C}$ , 10–16 h, (2) thionyl chloride, triphenylphosphine,  $\text{CH}_2\text{Cl}_2$ , 3 Å (0.3 nm) molecular sieves,  $0 \rightarrow 25^\circ\text{C}$ , 3 h; (b) 3 M HCl, MeOH,  $0 \rightarrow 25^\circ\text{C}$ , 3 h; (c) cat. *N,N*-dimethylaminopyridine, DBU,  $\text{CH}_2\text{Cl}_2$ ,  $25^\circ\text{C}$ , 18 h.

tide **38** ( $n = 1$ ) was removed to give the polymer-bound hydrazide **39**. This was then reacted with activated monomer **40** to give **38** ( $n = 2$ ). Using the polymer-bound solution phase methodology allowed for easy purification of the intermediates by precipitating the polymer-supported oligomers out of solution and washing with the appropriate solvent. This process was utilized to synthesize a pentamer **38** ( $n = 5$ ) with an overall yield of 57%.

A series of oligomers containing a vinylous sulfonamide linkage has been reported. The formation of oligomers has been de-

scribed using both solution (Gennari et al., 1994) and solid phase (Gennari et al., 1995) methodology. As shown in Scheme 1-13, the synthesis can be performed using divergent/convergent growth. However, the reports to date have only involved the addition of one monomer unit per repetition to the growing oligomer chain. Two steps were required for each cycle. Monomer **41** was synthesized in two steps from amino acids with a high yield (75–85%). Oligomer growth began by deprotection of the amine group to give **43**, and a portion of the monomer was converted to the sulfonyl

chloride **42**. Reaction of **42** and **43** gave **41** ( $n=2$ ). This scheme was used to synthesize oligomer **41** ( $n=4$ ) with an overall yield of 20–30%. The oligomer growth using the solid-phase approach was only used for the synthesis of dimers, with an overall yield of 52–75%.

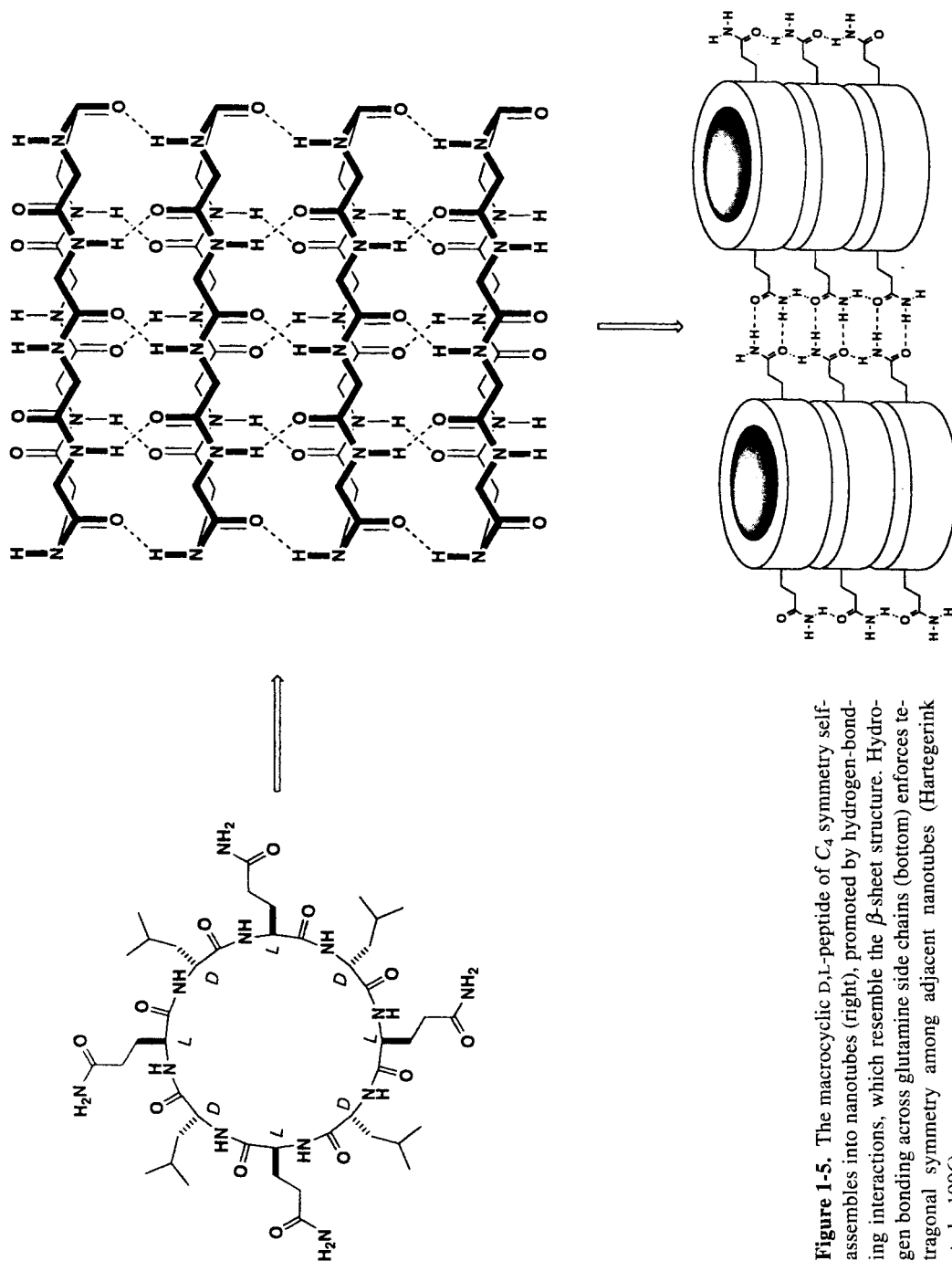
## 1.5 Architectures Derived from Sequence-Specific Oligomers

The diverse chemistry seen in the above synthetic survey reflects the wide range of scientific and technological areas in which nonbiological, structure-controlled oligomers are being studied. While homologous series of oligomers continue to provide fundamental understanding in the area of physical polymer chemistry, they have also had an impact on problems in materials science and molecular biology. Described below are a few selections that illustrate recent uses of sequence-specific oligomers in some of these areas.

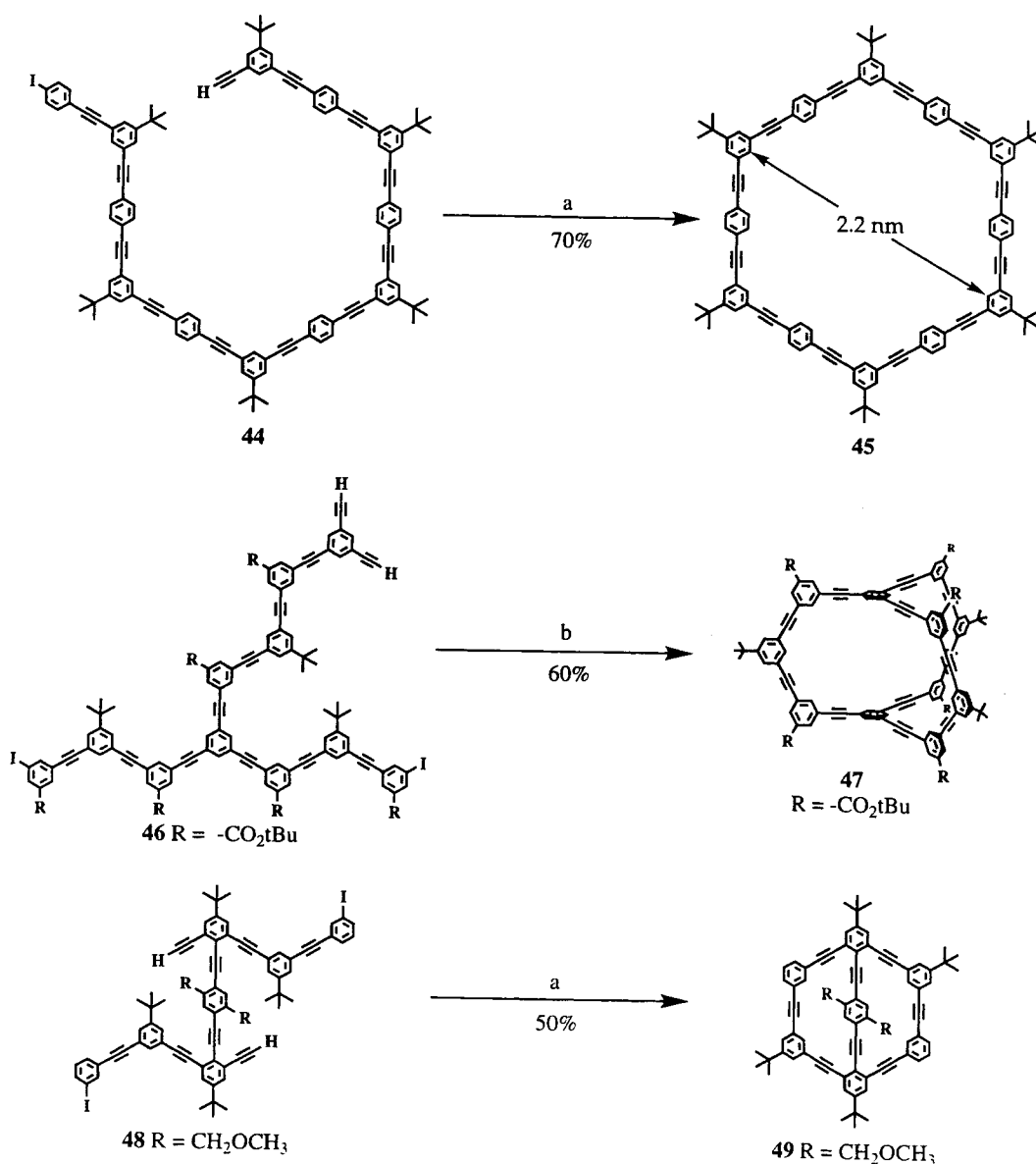
Structurally well-defined oligomers have long been used for the preparation of site-specifically functionalized and geometrically controlled macrocyclic compounds. A recent example is the peptide macrocycles derived from alternating oligomeric sequences of D- and L-amino acids prepared by Ghadiri and coworkers (Fig. 1-5) (Harterink et al., 1996). Interestingly, they showed that nanotubes spontaneously form from these macrocycles by a self-assembly process which utilizes  $\beta$ -sheet-like interactions between macrocyclic D,L-peptides. Structural studies based on electron diffraction data support the hypothesis that the 3D crystallographic organization is driven by nonspecific hydrophobic interactions between leucine side chains, as well as intertube hydrogen bonding between glutamine

side chains, leading to tetragonal packing of the nanotubes (Fig. 1-5). Nanotube packing is thus dictated by the  $C_4$  symmetry of the macrocycle. This example nicely illustrates the use of information-rich molecular precursors for the rational design of solids. This information can ultimately be traced to the oligomeric sequence that was used to construct the macrocycle.

Sequence-specific phenylene ethynylene oligomers have proven to be extremely valuable in the preparation of macrocycles such as **45** (Scheme 1-14). Dropwise addition of  $\alpha$ - $\omega$ -functionalized oligomers to an active solution of a palladium catalyst gives macrocycles in a good yield (Zhang et al., 1992, 1994). Macrobicycles such as **47** and **49** are readily prepared by double cyclization of branched sequences **46** and **48** (Wu et al., 1992; Bedard and Moore, 1995). Many of the macrocycles prepared by these methods have shown interesting and sometimes unique behavior. One surprising observation was the discovery that hexaphenylacetylene macrocycles aggregate in solution to a degree that is readily observable by  $^1\text{H}$  NMR (Shetty et al., 1996). While the geometry of these aggregates is not known for certain, a series of structural studies strongly suggest the formation of stacked rings. These findings led to the discovery of columnar liquid crystal phases based on these toroidal-shaped mesogens (Zhang and Moore, 1994), showing that these shape-persistent macrocycles are capable of producing noncollapsible “tubular” mesophases. Finally, molecular turnstile **49** was designed with the intention of creating a system that exhibited conformational bistability. NMR data showed that rotation of the disubstituted spindle of **49** about its para axis is slow on the experimental time scale at sub-ambient temperatures, but this motion becomes rapid at elevated temperatures (Bedard and Moore, 1995).



**Figure 1-5.** The macrocyclic D,L-peptide of  $C_4$  symmetry self-assembles into nanotubes (right), promoted by hydrogen-bonding interactions, which resemble the  $\beta$ -sheet structure. Hydrogen bonding across glutamine side chains (bottom) enforces tetragonal symmetry among adjacent nanotubes (Hartgerink et al., 1996).



**Scheme 1-14.** Site-specifically functionalized and geometrically controlled macrocycles derived from oligomeric phenylene ethynylene (Zhang et al., 1994). Reagents: **(a)** bis(dibenzylideneacetone)palladium(0), cuprous iodide, triphenylphosphine, triethylamine, 70 °C; **(b)** bis(dibenzylideneacetone) palladium(0), cuprous iodide, triphenylphosphine, triethylamine, benzene, 70 °C.

The motivation for synthesizing and studying many of the heteroatom-containing oligomers (e.g., Fig. 1-4 and Schemes 1-8 to 1-13) stems largely from their similarity to natural biopolymers (i.e., peptidomimetics,

DNA mimetics). However, these oligomers typically have the added benefit of enhanced metabolic stability, which makes them viable candidates for medicinal applications. For example, peptide nucleic acids (PNAs,

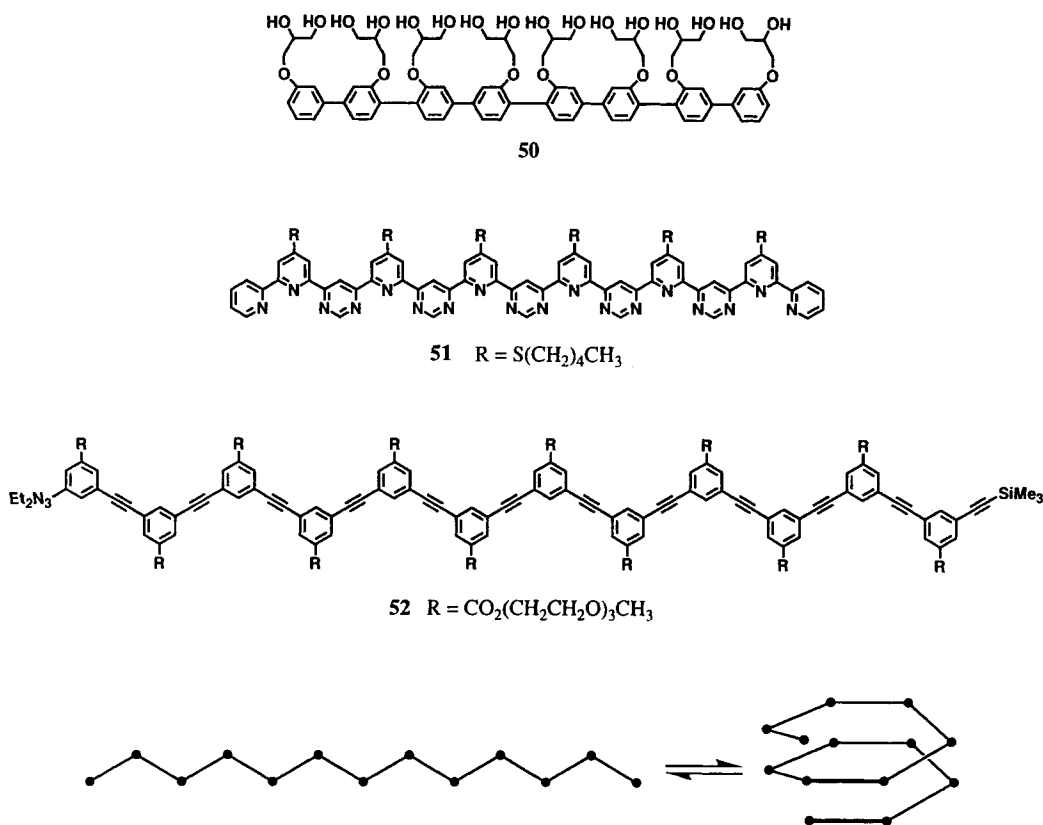
Fig. 1-4) are DNA mimetics derived from a pseudopeptide backbone composed of *N*-(2-aminoethyl)glycine units, with nucleobases attached to the glycine nitrogen via carbonyl methylene linkers. PNAs were first reported in 1991 (Nielsen et al., 1991) and have since attracted broad attention within the fields of bioorganic chemistry, medicinal chemistry, physical chemistry, and molecular biology due to their chemical and physical properties, especially with regard to sequence-specific binding to both single-stranded RNA and DNA, as well as to double-stranded DNA (Nielsen et al., 1994; Nielsen and Haaime, 1997; Dueholm and Nielsen, 1997). Another type of DNA-binding polyamide has been reported by Dervan and coworkers (Trauger et al., 1996). Their design incorporated a pair of rigid, short-segment oligomers of *N*-methylimidazole and *N*-methylpyrrole amino acids connected by a short flexible spacer, which allowed the two rigid segments to fold back against one-another. This folded motif was shown to bind in the minor groove of DNA with high sequence specificity. Oligomers such as these, which can specifically bind with high affinity to any predetermined DNA sequence in the human genome, will be useful tools in molecular biology and potentially in human medicine.

There has been considerable activity in attempting to design nonbiological oligomers that spontaneously acquire a well-defined secondary structure (i.e., "foldamers"). Gellman (Gellman et al., 1996, 1997) and Seebach (Hintermann and Seebach, 1997a; Seebach et al., 1996a) have independently shown that stable  $3_1$ -*M*-helical structures are realized in short  $\beta$ -peptide sequences (Fig. 1-4). This is in contrast to the  $3.6_1$ -*P*-helix typical of  $\alpha$ -peptides. The driving force for the  $3_1$ -*M*-helix is the formation of a cyclic 14-membered hydrogen bond (H-bond) motif, which is comparable to the

13-membered cyclic H-bonded motif of  $\alpha$ -peptides. Interestingly, the solution stable secondary structures of  $\beta$ -peptides are realized for oligomers containing as few as six  $\beta$ -amino acid residues. Seebach has reported that these oligomers do not have mutagenic properties, and yet they are resistant to peptidase degradation (Hintermann and Seebach, 1997b).

In addition to foldamers derived from H-bond interactions, there have been a few reports on secondary structures driven by less specific noncovalent interactions (Lokey and Iverson, 1995; Nelson et al., 1997; Bassani et al., 1997). H-bonded structures that are stable in nonpolar solvents often disintegrate in aqueous solution because of solvent competition (Lawrence et al., 1995). In proteins, hydrophobic interactions and compaction due to hydrophobic collapse undoubtedly also play a role in guiding helix formation (Dill et al., 1995). Unlike H-bonds, hydrophobic and van der Waals interactions are less selective and directionally specific, a point that has dissuaded their use in the design of conformational uniqueness (Whitesides et al., 1991). However, in 1995 Lokey and Iverson reported that aedamers (Fig. 1-4) fold in water into a pleated secondary structure as a result of interactions between alternating electron-rich donor groups and electron-deficient acceptor groups. While this work represents a significant achievement, these secondary structures, like the  $\beta$ -peptides described above, lack a functional motif (e.g., for binding, molecular transport, or catalysis). An important area for further study appears to be the invention of foldamers that capture not only the basic structural features of proteins, but also the functional characteristics as well.

For functions that require a cavity, two oligomer-based supramolecular approaches can be envisioned. The first approach in-



**Figure 1-6.** Examples of oligomers with potential functional capabilities. Membrane-spanning oligophenylene **50** is postulated to form an ion channel in bilayer membranes (Sakai et al., 1997). Heteroaromatic oligomer **51** adopts a helical conformation in solution and in the solid state forming a 2.6 Å (0.26 nm) diameter channel (Bassani et al., 1997). The presumed conformational equilibrium is shown at the bottom of the figure. This same equilibrium governs dodecamer **52**, which is driven into a helical conformation in solution by solvents that poorly solvate the nonpolar backbone (Nelson et al., 1997). Molecular models show that the internal diameter of the helix formed from **52** is ca. 6 Å (0.6 nm).

volves intermolecular aggregation of an oligomeric bundle. This mechanism might be responsible for the transport properties seen in the artificial ion channels derived from oligo(*p*-phenylenes) **50** (Fig. 1-6) (Sakai et al., 1997). The second approach involves the design of oligomers that fold into conformations to create large helical cavities. Two recently reported examples shown in Fig. 1-6 are Lehn's (Bassani et al., 1997) heteroaromatic oligomer **51** and Moore's (Nelson et al., 1997) oligo(phenylene ethynylenes) **52**. In the case of **51**, long-range conformational order is achieved in

solution as well as in the solid state by the preference of adjacent pyridine-pyrimidine rings to adopt a *transoid* conformation. In the solid state, the helical form possess a 2.6 Å (0.26 nm) diameter interior void, as determined by X-ray crystallography. The crystal structure shows that the helical molecules are stacked one above the other along a common axis, thus forming long channels which might be of interest for ion channel design. In the case of **52**, the basic design involves attaching polar side groups to a nonpolar aromatic backbone. The postulated helical secondary structure is real-



ized from a conformation in which the oligomer folds back upon itself, such that the aromatic rings stack face-to-face along the helix axis. This conformation maximizes the interactions between the polar solvent and the polar side groups; it maximizes aromatic contacts and minimizes unfavorable interactions between the solvent and the hydrocarbon backbone. The chain does not form intramolecular hydrogen bonds, and solvophobic interactions drive the folding transition, which is sensitive to chain length, solvent quality, and temperature (Nelson et al., 1997). These solvophobically driven helical structures produce a cavity with a large [ca. 6 Å (0.6 nm)] internal diameter, which may be capable of binding substrates or metal ions once properly functionalized.

The role of a secondary structure in nonbiological oligomers may have important implications for problems in materials chemistry as well. For example, Berg et al. (1996) reported that a presumed helical architecture adopted by DNO oligomers (Fig. 1-4) is ideally suited for generating light-driven holographic gratings. Their design is based on the notion that azobenzene chromophores oriented around a helical axis all have their transition moments perpendicular to the axis direction. It was previously found that photoisomerization of azobenzene chromophores in polymeric glasses with polarized radiation resulted in light-induced chromophore orientation (perpendicular to the polarization direction). The DNO backbone thus serves as a scaffolding that could impose a self-reinforcing orientational order on the chromophores, thereby optimizing the optical response. Although there was little evidence provided to show that the presumed helical structure was realized, materials with large, stable first-order diffraction efficiencies were achieved.

## 1.6 Conclusions

Over seven decades ago, oligomers of formaldehyde played a vital role in establishing the covalent character of macromolecules. Today, nonbiological oligomers continue to add to our understanding of the physical behavior of macromolecules, especially in the area of supramolecular polymer chemistry. It is increasingly apparent that unique architectures can be realized from oligomeric compounds, especially through combinations of covalent design and intramolecular self-organization. These novel architectures are opening new vistas in supramolecular chemistry, materials science, and molecular biology. At the foundation of these molecular designs are well-controlled repetitive synthetic sequences, many of which were outlined earlier. As the role of oligomers in many areas of the molecular sciences expands, there is a clear need for the continued development of new and more efficient repetitive synthetic methods. Oligomers of today, and those of tomorrow, are no longer the forgotten middle child.

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## 2 Transition Metal-Catalyzed Polycondensation and Polyaddition

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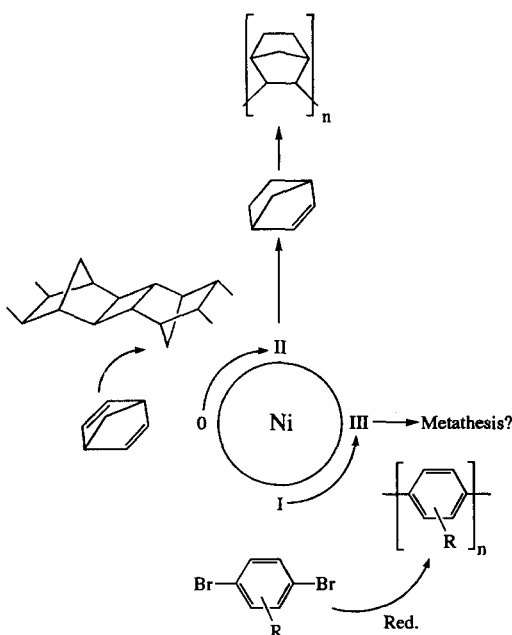
## List of Symbols and Abbreviations

$L$	ligand
$m$	number
$M$	molecular weight
$n$	number
$T$	temperature
$x$	number
$y$	number
$\eta_{\text{inh}}$	inherent viscosity
$\lambda$	wavelength
AB	absorption
Ac	acetyl
bipy	2,2'-bipyridyl
Bog	Bogdanovic
Bu	butyl
CD	circular dichroism
cp	cyclopentadiene
CPA	chloroplatinic acid
dba	dibenzylidene acetone
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
dcypb	1,4-bis(dicyclohexylphosphino)butane
dippb	1,4-bis(diisopropylphosphino)butane
DMAc	dimethylacetamide
DMF	dimethylformamide
dppp	1,3-bis(diphenylphosphino)propane
EL	electroluminescence
Et	ethyl
LC	liquid chromatography
LDA	lithium di- <i>i</i> -propylamide
LED	light-emitting diode
NLO	nonlinear optical
NMR	nuclear magnetic resonance
Ph	phenyl
PL	photoluminescence
PPP	poly- <i>p</i> -phenylene
Pr	propyl
quin	quinoline
Tf	triflate
THF	tetrahydrofuran
TMEDA	tetramethylethylenediamine
top	tri- <i>o</i> -tolylphosphine
tpp	triphenylphosphine

## 2.1 Introduction

Metal-catalyzed polymerizations (chain growth reactions) are key technologies of polymer synthesis nowadays. A rapid increase of knowledge has occurred, starting with the discoveries of Ziegler (Ziegler, 1964; Ziegler et al., 1955) and Natta (Natta, 1959; Natta et al., 1955), and the strong push in that area by Kaminsky and Brintzinger (Kaminsky et al., 1985), caused by the development of metallocene initiation (Fink et al., 1995; Soga and Terano, 1994). A driving force here is a better understanding of organometallic complexes and chemistry (Collman et al., 1997; Hegedus, 1995; Togni and Hayashi, 1995; Heck, 1987; Liebeskind, 1989; Percec and Hill, 1996). This has also prompted activities to prepare polymers by metal-catalyzed polycondensation and polyaddition reactions (step growth reactions) (de Meijere and Meyer, 1994). Metal-catalyzed polymerization reactions are

chain reactions with a organometallic end group, and require a constant metal valence. According to this definition, redox polymerizations are not considered as metal-catalyzed polymerizations; the metal is not participating in the chain growth reaction. Polycondensations and polyadditions feasible by metal catalysis are step growth reactions involving a change of the valence of the metal. This change of valence is predominantly a two-electron process [ $\text{Pd}(0) \rightleftharpoons \text{Pd}(\text{II})$ ,  $\text{Ni}(0) \rightleftharpoons \text{Ni}(\text{II})$ ,  $\text{Ni}(\text{I}) \rightleftharpoons \text{Ni}(\text{III})$ ]. Therefore a single metal usually allows a variety of reactions (Fig. 2-1).  $\text{Ni}(\text{II})$  complexes are able to polymerize butadiene (Hadjianandrou et al., 1984; Faza et al., 1997), norbornene (Faza et al., 1997; Goodall et al., 1995), or ethylene (Brookhardt et al., 1995).  $\text{Ni}(0/\text{II})$  allows for a polyaddition reaction by a  $[2+2]$  cycloaddition.  $\text{Ni}(\text{I}/\text{III})$  is involved in the polycondensation to polyphenylenes.

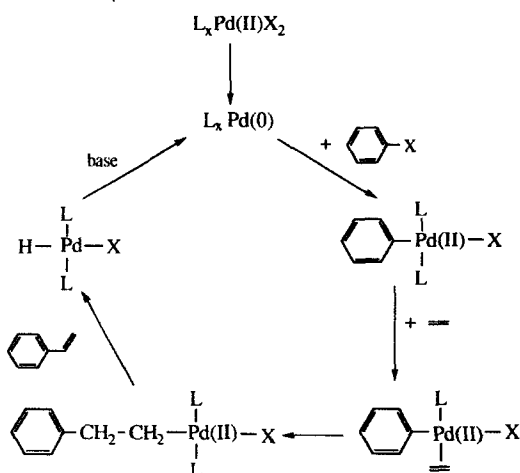


**Figure 2-1.** Polyreactions of nickel in different oxidation states.

## 2.2 Polycondensation Reactions

### 2.2.1 Model Reactions and Mechanistic Considerations

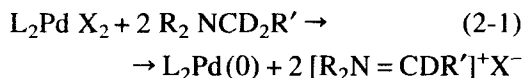
In metal-catalyzed addition reactions, the oxidative addition and the reductive elimination are key steps. With the catalytic cycle of the Heck reaction, it is easy to exemplify how we can tune the reaction towards polyaddition or polymerization (Scheme 2-1). Starting from  $\text{Pd}(0)$ , the oxidative addition of, e.g., bromobenzene, results in a  $\text{Pd}(\text{II})$  species. The next steps are the coordination and insertion of an olefin. Decisive for tuning the reaction is the subsequent  $\beta$ -H elimination, we are in a position to develop a catalyst for polymerization. These catalysts typically have a big gegenion (Sen et al., 1988), e.g.,  $\text{BF}_4^-$ ,  $\text{SbF}_6^-$ . A typical example of a monomer is norbornene (Mehler and



Scheme 2-1.

Risse, 1992; Haselwander et al., 1996).  $\beta$ -H elimination after the insertion would result in ring strain. The insertion of ethylene is usually followed by  $\beta$ -H elimination. However, in the presence of CO the CO insertion is faster than the  $\beta$ -H elimination. Perfectly alternating copolymers of ethylene-carbonmonoxide are then available (Zhao and Chien, 1992; Abu-Surrah et al., 1996). In the Heck type reaction, the leaving group is given by the  $\text{ArX}$  used. Polymerization catalysts usually have a weakly or non coordinating anion, i.e., the active center for polymerization is a cation in the catalytic cycle.

The reduction of the  $\text{Pd(II)}$  species to the  $\text{Pd(0)}$  catalyst is favored by many bases. In most preparative procedures, a  $\text{Pd(II)}$  salt is used as the starting compound. The conversion to  $\text{Pd(0)}$  is given in situ, e.g., by reaction with amines, as shown by deuterating experiments (Brenda et al., 1990) (Eq. 2-1).

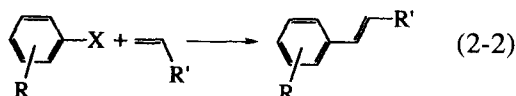


However, the reaction of  $\text{Pd(II)}$  to  $\text{Pd(0)}$  can also give rise to side reactions, causing defects in the polymer chain. The vinylation of aryl iodides is also catalyzed by cobalt,

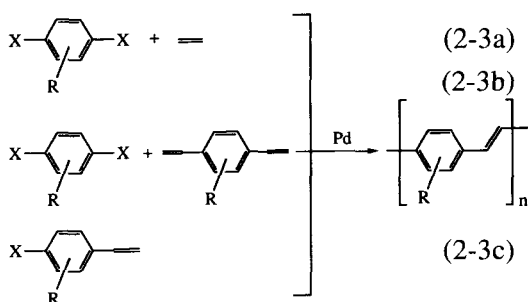
rhodium and iridium complexes (Iyer, 1995).

### 2.2.1.1 Removing HX

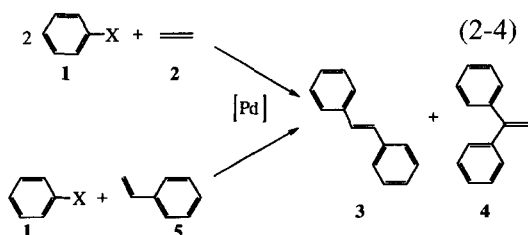
The use of the Heck reaction is one of the earliest examples of preparing a tractable poly(phenylene vinylene) derivative by a metal-catalyzed reaction (Greiner and Heitz, 1988; Heitz et al., 1988). The growing interest in this polymerization stems from the fact that it is an LC polymer when completely trans configured, and it is an excellent emitter in polymeric light-emitting diodes (Burn et al., 1992; Vestweber et al., 1993).



In the Heck reaction, a variety of substituents are tolerated. X usually represents iodine, bromine, chlorine, and triflate. Iodine does not need a ligand for the palladium catalyst. Oxidative addition of the other starting compounds requires reaction conditions where the palladium has to be stabilized by ligands. The oxidative addition of the chloroarenes requires higher temperatures and  $\text{dppb}$  as the ligand (Ben-David et al., 1992). The reactivity of olefin decreases in the order  $\text{arcylate} > \text{ethylene} > \text{styrene}$ . Electron-withdrawing substituents R at the aryl compound enhance the rate of reaction. Although DMF is mostly used as the solvent, it is possible to perform the reaction in THF, toluene, cyclohexane, alcohol, or biphasic (toluene/water). The use of tert amines and inorganic bases is described: The ligands used are mono- and bidentate phosphines, amines, and dibenzylidene acetone (Klingelhöfer, 1996). Heck recommends the use of tri-*o*-tolylphosphine to suppress transarylation by the phosphine. The synthesis of poly(phenylene vinylene) can be accomplished in different ways (Eq. 2-3 a-c).



The reaction with ethylene is fast, requiring only a fraction of the total reaction time. As a consequence, the main structure stems from a reaction according to Eq. (2-3c) with R in m-position to vinyl. Starting from divinyl arenes, it is possible to prepare alternating copolymers. Specifically the use of these materials for electrooptical purposes stimulated model reactions in order to minimize and quantify defect structures.



The reaction is completely stereoselective. Only *trans*-stilbene is formed (Eq. 2-4). All reports on the formation of *cis*-stilbene in the literature can be disproved. The side product is 1,1-diarylstilbene. Therefore the problem of the reaction is its regioselectivity. Under the usual conditions of the Heck reaction, the selectivity (1.2/1.1 ratio) is about 95/5 (Table 2-1).

The selectivity increases with decreasing temperature. Higher regioselectivity is also observed by adding LiCl or using  $\text{Ag}_2\text{CO}_3$  as the base. Triflate as the leaving group results in a loss of the selectivity. This is explained by the formation of a cationic  $\text{Pd}^+$  intermediate (Cabri and Candiani, 1995). As a consequence, an increase in selectivity  $\text{J} < \text{Br} < \text{Cl}$  should be expected. However, the temperature required for oxidative addition increases in the same order, which is contraproductive for higher selectivity. With diazonium salts, the oxidative addition is possible at room temperature. High regioselectivities are obtained with chlorine as well as triflate as the leaving group (99/1). This result is not compatible with the assumption that cationic species are responsible for a change of the regiocontrol of the reaction.

**Table 2-1.** Comparison of the ratio of 1,1-substituted olefins versus 1,2-substituted olefins obtained by palladium-catalyzed coupling with different reaction conditions [Eq. (4 a/b)].

Olefin	X	Reaction characteristics <sup>1</sup>	Yield 3 (%) <sup>2</sup>	Ratio (3/4) <sup>3</sup>
2	Br	140 °C, $\text{NEt}_3$ , tpp	57	86/14
2	Br	100 °C, $\text{NEt}_3$ , top	88	94/ 6
2	Br	50 °C, $\text{NEt}_3$ , top	91	97/ 3
2	Br	100 °C, $\text{NEt}_3$ , top, LiCl	97	97/ 3
5	Br	100 °C, $\text{NEt}_3$ , top, LiCl	98	98/ 2
5	I	70 °C, $\text{Ag}_2\text{CO}_3$	78	99/ 1
5	Cl	100 °C, NaOAc, dcyph	66	95/ 5
5	$\text{O}_2\text{CCF}_3$	70 °C, $\text{NEt}_3$ , dppp	52	58/42
5	$\text{N}_2^+\text{Cl}^-$	25 °C, $\text{NBu}_3$ , $\text{Pd}(\text{dba})_2$ , toluene, $\text{H}_2\text{O}$	91	99/ 1
5	$\text{N}_2^+\text{O}_2\text{CCF}_3^-$	25 °C, $\text{NBu}_3$ , $\text{Pd}(\text{dba})_2$ , toluene, $\text{H}_2\text{O}$	91	99/ 1

<sup>1</sup> Reactions were performed with  $\text{Pd}(\text{OAc})_2$  as the catalyst; <sup>2</sup> the yields of 3 were determined gas chromatographically using internal standards; <sup>3</sup> the ratio of 3/4 was determined by gas chromatography.



**Table 2-2.** Comparison of the ratio of 1,1-substituted olefins versus 1,2-substituted olefins obtained by palladium-catalyzed coupling with different reaction conditions [Eq. (5a/b)].

Olefin	X	R	Reaction characteristics <sup>1</sup>	Yield <sup>2</sup> of <b>8</b> or <b>10</b> (%)	Ratio <sup>3</sup> ( <b>8/9</b> ) or <b>10/11</b>
<b>2</b>	Br	C <sub>6</sub> H <sub>5</sub>	100 °C, NEt <sub>3</sub> , top	61	70/30
<b>2</b>	Br	CH <sub>3</sub>	100 °C, NEt <sub>3</sub> , top	72	87/13
<b>2</b>	Br	CF <sub>3</sub>	100 °C, NEt <sub>3</sub> , top	85	95/ 5
<b>5</b>	Br	2-ethylhexyloxy	100 °C, NBu <sub>3</sub> , top	45	91/ 9
<b>5</b>	Br	2-ethylhexyloxy	100 °C, NBu <sub>3</sub> , top, LiCl	44	95/ 5
<b>2</b>	Br	2-ethylhexyloxy	100 °C, NBu <sub>3</sub> , top	42	61/39
<b>2</b>	Br	2-ethylhexyloxy	100 °C, NBu <sub>3</sub> , top, LiCl	50	64/36
<b>5</b>	Br	C <sub>6</sub> H <sub>5</sub>	100 °C, NBu <sub>3</sub> , top	83	94/ 6
<b>5</b>	Br	C <sub>6</sub> H <sub>5</sub>	100 °C, NBu <sub>3</sub> , top, LiCl	83	97/ 3
<b>2</b>	Br	C <sub>6</sub> H <sub>5</sub>	100 °C, NBu <sub>3</sub> , top	48	60/40
<b>2</b>	Br	C <sub>6</sub> H <sub>5</sub>	100 °C, NBu <sub>3</sub> , top, LiCl	52	72/28
<b>5</b>	N <sub>3</sub> <sup>+</sup> Cl <sup>-</sup>	C <sub>6</sub> H <sub>5</sub>	25 °C, NBu <sub>3</sub> , Pd(dba) <sub>2</sub> <sup>4</sup>	72	99/ 1
<b>5</b>	N <sub>3</sub> <sup>+</sup> Cl <sup>-</sup>	OCH <sub>3</sub>	25 °C, NBu <sub>3</sub> , Pd(dba) <sub>2</sub> <sup>4</sup>	77	99/ 1

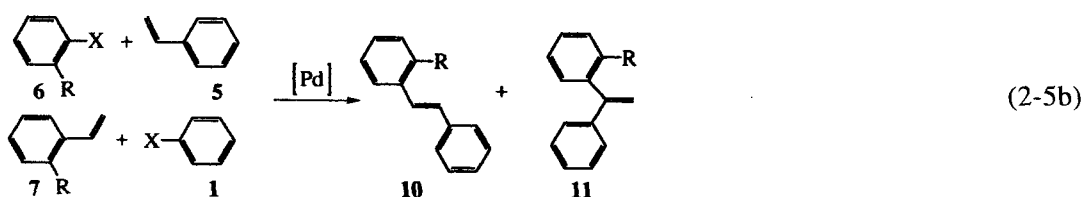
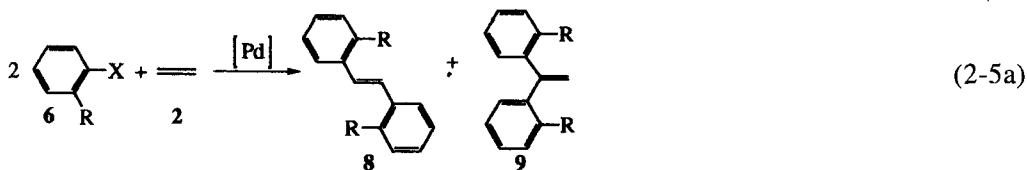
<sup>1</sup> Reactions were performed with Pd(OAc)<sub>2</sub> as the catalyst; <sup>2</sup> the yields of **8** or **10** were determined by isolation of the products (1,2-product and 1,1-product) and comparison with the gas chromatographically determined ratio of 1,2-product/1,1-product; <sup>3</sup> the ratio of **8/9** or **10/11** was determined by gas chromatography;

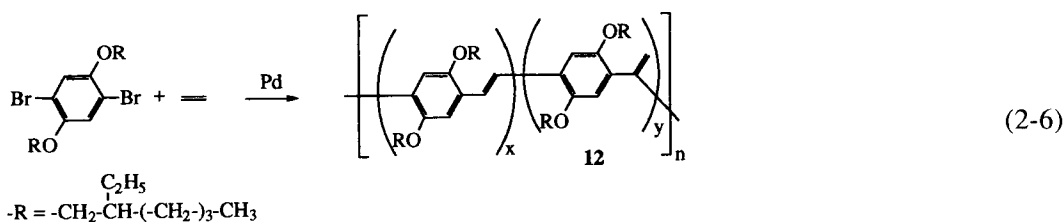
<sup>4</sup> toluene/H<sub>2</sub>O.

Substituents in the *o*-position of styrene have a strong influence on the reaction. In Eq. 2–5a ethylene reacts fast to form an *o*-substituted styrene. Disubstitution occurs with low regioselectivity. Reacting *o*-substituted halogenoarenes or diazonium salts with styrene results in good regioselectiv-

ities (Table 2-2), but the selectivity in the conversion of 2-(2-ethyl hexyloxy)styrene with bromo benzene is 77/23.

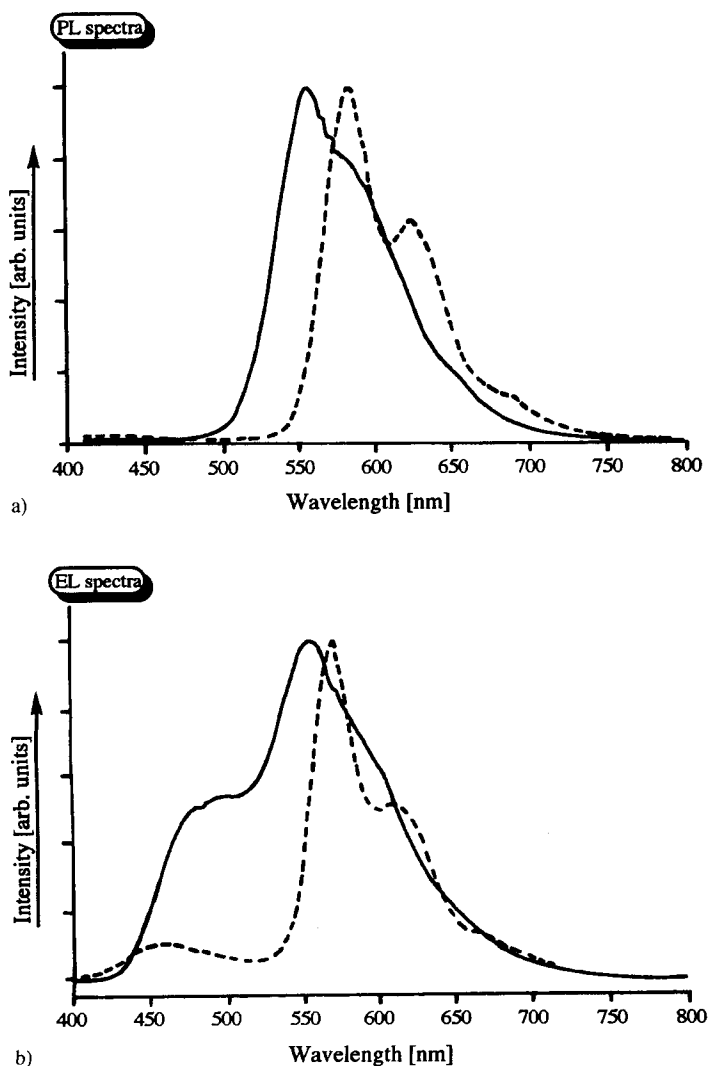
The results of these model reactions are reflected in the structure of poly(phenylene vinylene)s prepared by the Heck reaction (Klingelhöfer et al., 1997).



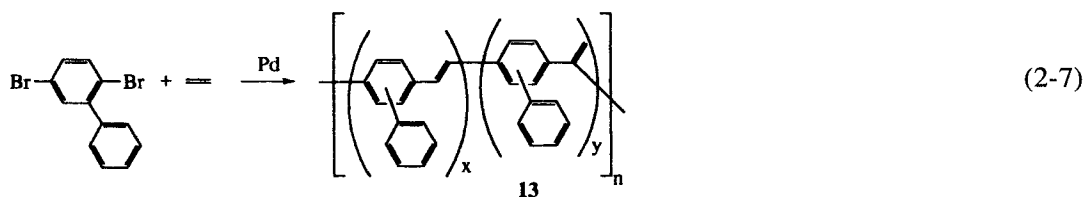


Starting from 1,4-dibromo-2,5-di(oxy-2-ethylhexyl)benzene and ethylene, the fraction of 1,1-disubstitution in the polymer is so high that the average conjugation length is lower than that of defect-free polymer

(Eq. 2-6). This is evident from the absorption, fluorescence, and photoluminescence spectra compared to those of the same polymer prepared by the Suzuki reaction (Fig. 2-2).

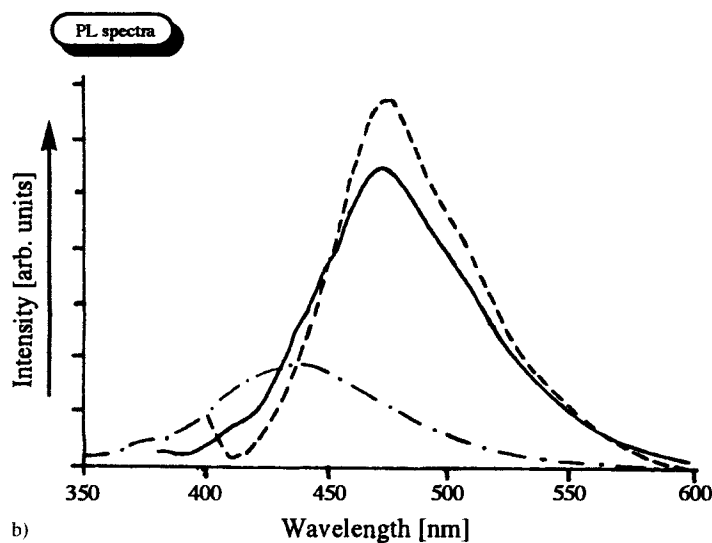
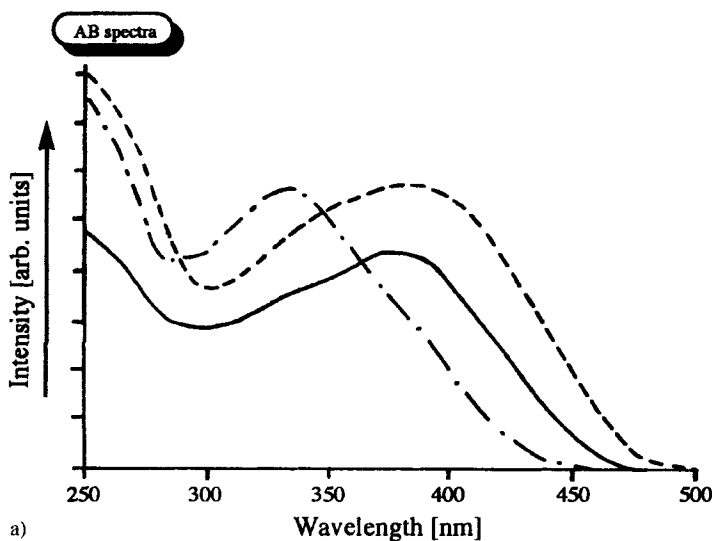


**Figure 2-2.** Photoluminescence (2a) and electroluminescence (2b) spectra of PPV 12 prepared by the Heck reaction (—) and the Suzuki reaction (----).

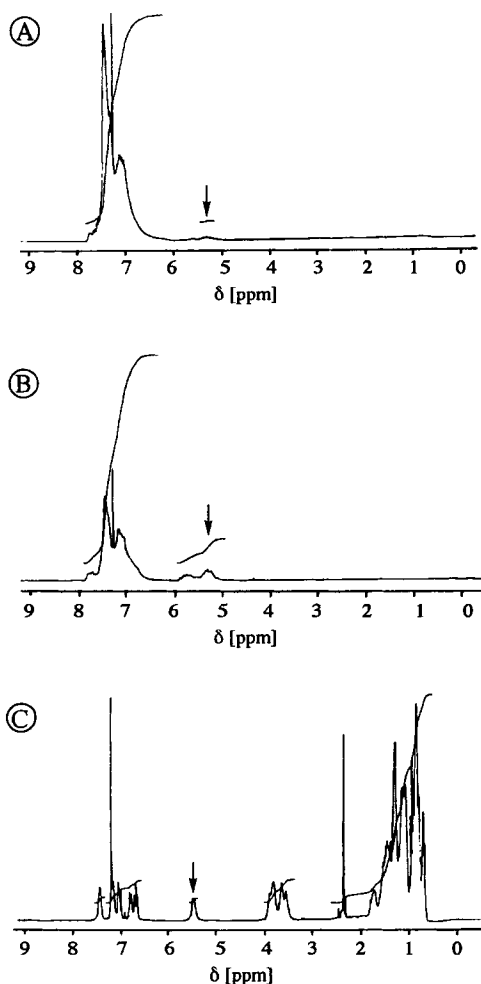


The reactivity of the two bromines in 2,5-dibromo biphenyl is different. The 5-bromo substituent reacts first (Eq. 2-7). The pre-

dominant intermediate is a styrene, which is not substituted in the *o*-position. As a result, the fraction of 1,1-disubstitution is so low that



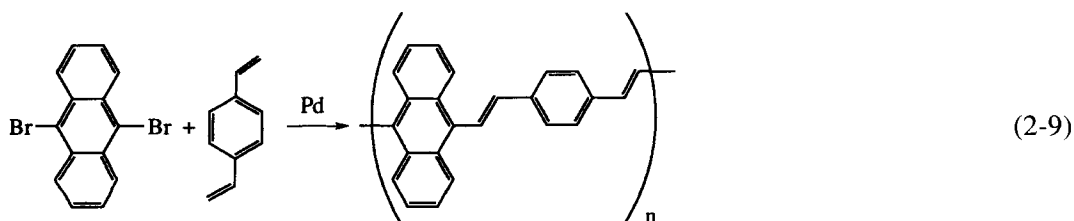
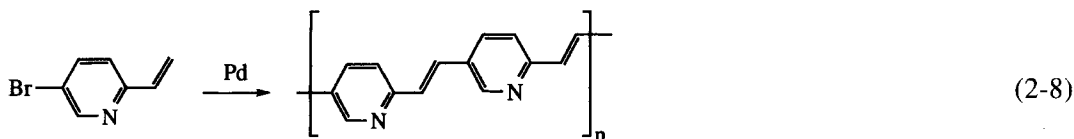
**Figure 2-3.** Absorption (3 a) and photoluminescence (3 b) spectra of PPV 12 prepared by the Heck reaction (—) using dibromo compounds and using bistriflates (— · — ·) and the Suzuki route (----).

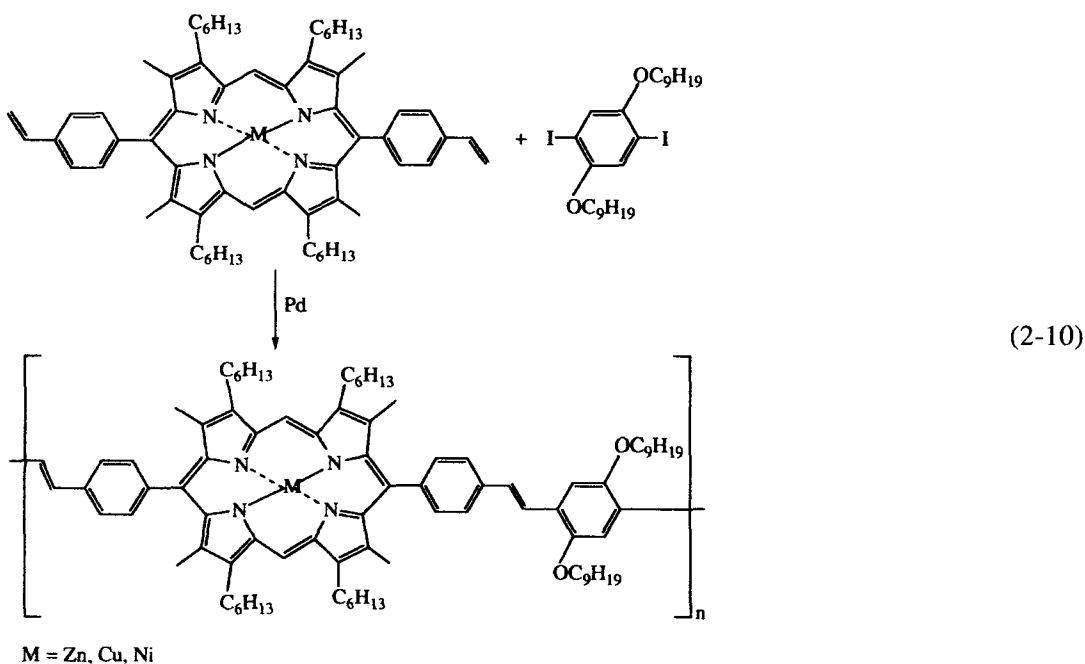


**Figure 2-4.**  $^1\text{H}$ -NMR of PPV 12 prepared by the Heck reaction using dibromo compounds (A) and using bistriflates (B), and PPV 11 prepared by the Heck reaction (C).

it is at the detection limit of NMR and there is no difference in the optical properties compared to those of the polymer obtained by the Suzuki reaction (Fig. 2-3). Starting from the corresponding triflate, the fraction of 1,1-disubstitution is quite high, as revealed by NMR (Fig. 2-4) and in agreement with the model reaction.

By the Heck reaction a variety of soluble poly(phenylene vinylene)s was prepared which were substituted with  $\text{CH}_3$ ,  $\text{CF}_3$ , alkyl, and oxyalkyl groups (Greiner and Heitz, 1988; Heitz et al., 1988; Klingelhöfer et al., 1997; Bao et al., 1993). Poly(pyridyl vinylene) with a regiochemically pure head–tail structure was obtained by the same method (Marsella et al., 1995a) (Eq. 2-8). The tuning of the optical properties was achieved by the combination of different chromophores (Eq. 2-9 and 2-10) (Weitzel et al., 1990; Bao et al., 1994; Greiner et al., 1996).



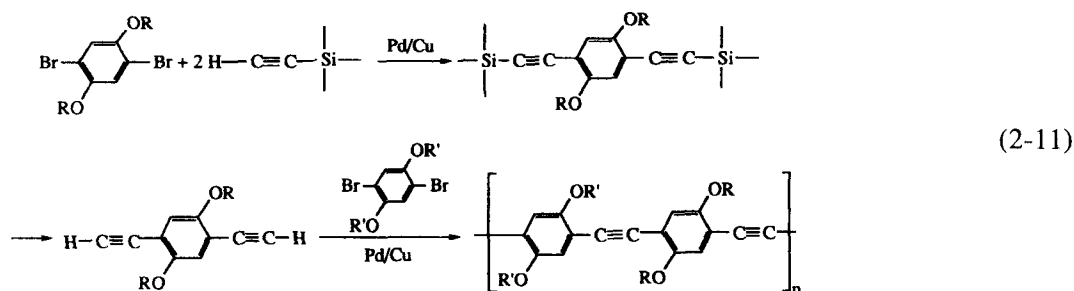


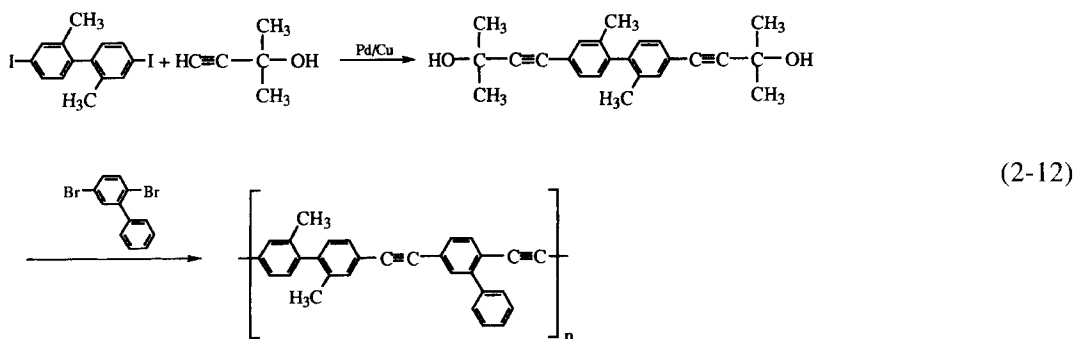
Polycinnamamides were prepared by Palladium-catalyzed reaction of bisacrylamides with diiodides (Imai, 1992).

The synthesis of poly(phenylene ethynylene) by a palladium/copper-catalyzed reaction was described by Trumbo and Marvel (1986) using the procedure of Hagihara (Sonogashira et al., 1975). The solubility problems of the para structure were reduced by synthesis of the meta products. Soluble para-connected poly(phenylene ethynylene) was synthesized by Giesa and Schulz in

1990. Trimethylsilylacetylene has been used to avoid the preparative problems of stoichiometric use of acetylene (Eq. 2-11).

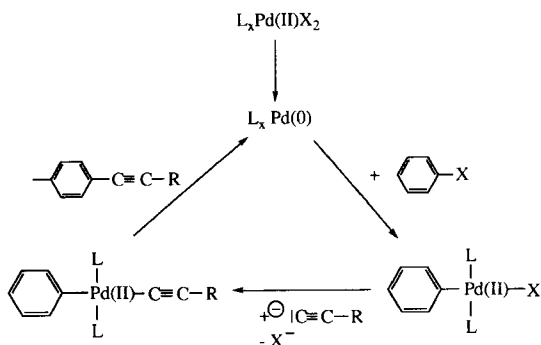
Using the same synthetic approach, a wide variety of structures from this class of polymers was obtained. The soluble polymers were mainly investigated with respect to their NLO and conducting properties (Moroni et al., 1994; Sanechika et al., 1984). The exponent 1.92 obtained in the viscosity molecular weight relationship confirms the rod-like structure of these polymers.





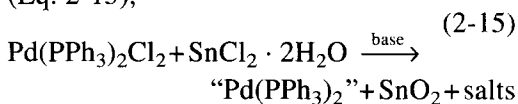
The adduct of acetylene and acetone allows simple synthesis of poly(phenylene ethynylene) (Solomin and Heitz, 1994). The absorption, photo-, and electroluminescence of these polymers are slightly blue-shifted compared to those of poly(phenylene vinylene). This absorption is reached at a polymerization degree of 7–8.

The catalytic cycle of this aryl/alkyne cross-coupling reaction involves oxidative addition and reductive elimination, as in the Heck reaction. A trans metallation instead of insertion, however, is discussed as more likely occur (Pugh and Percec, 1990). It is possible to have direct anion exchange ( $\text{X}^-$  vs.  $\text{C}\equiv\text{C}-\text{R}$ ). Using a copper-free palladium catalyst makes this an easy assumption (Scheme 2-2).

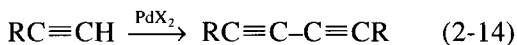
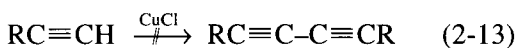


Scheme 2-2.

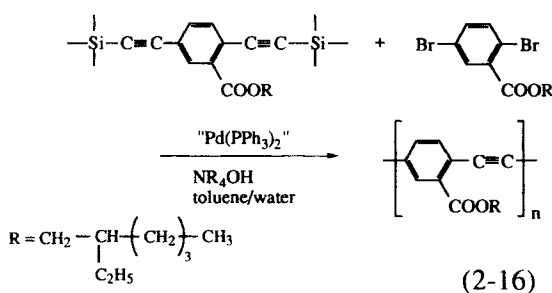
reactive catalyst solution can be obtained (Eq. 2-15),



which is not water-, but air-sensitive. Working in the presence of aqueous bases,  $\text{SnO}_2$  and salts can be removed. If this catalyst solution is added to the reaction mixture containing arylalkynes, in addition to the normal reaction, diene formation and oligomerization of the acetylene compound are observed. Meanwhile the bromo compound is not quantitatively consumed. This is a result of the high acetylide concentration during the reaction. If acetylide is gradually generated during the reaction, the ethinylation proceeds without detectable amounts of side reaction (Eq. 2-16).



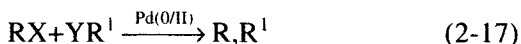
The major defect structure in this synthesis is the diene. This side product is not formed with  $\text{CuCl}$  (Eq. 2-13), as long as oxygen is strictly excluded under the usual reaction conditions, whereas  $\text{Pd(II)}$  is readily reduced, forming the diene [Häger and Heitz (1998), Eq. 2-14].  $\text{Pd(0)}$  ( $\text{PPh}_3$ )<sub>4</sub> has a low catalytic activity. By reduction of  $\text{Pd}(\text{tpp})_2\text{Cl}_2$  with  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , a highly



The resulting poly(phenylene ethynylene) containing ester can be converted to a rod-like polyelectrolyte.

### 2.2.1.2 Removing XY

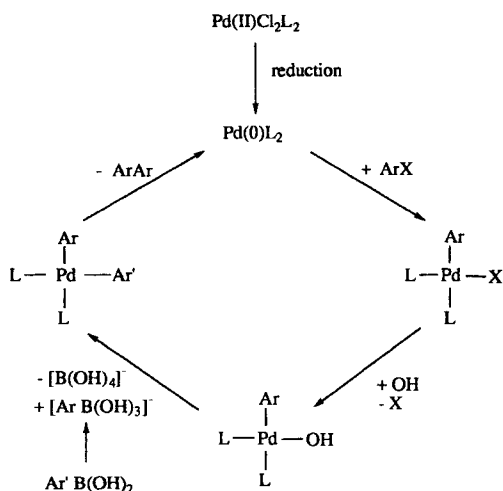
Carbon-carbon bond formation can also be accomplished by reacting RX with vinyl or aryl boronic acids [Suzuki type reactions (Suzuki, 1982, 1991)] or with organotin reagents [Stille type reactions (Stille, 1985;



where R, R<sup>1</sup> = vinyl or aryl,  
 X = halogen, triflate,  
 Y = B(OH)<sub>2</sub>, SnR<sub>3</sub>.

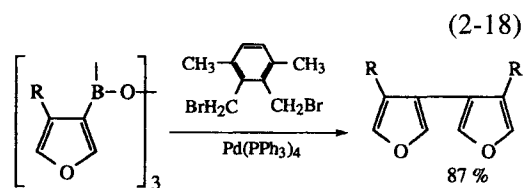
Mitchell, 1992)] in a palladium-catalyzed reaction (Eq. 2-17). the catalytic cycle involves Pd(0/II) (Scheme 2-3).

Phosphines or dibenzylidene acetone (dba) are typical ligands to palladium (Wallow and Novak, 1994). In the Suzuki reaction, deboronation is a typical side reaction. This can be reduced by using anhydrous bases in nonaqueous solvents (Watanabe et al., 1992). Another side reaction is transarylation. This may cause defect structures in the polymer or act as a chain-limiting reaction. In transarylation, the aryls from the phosphine ligands get involved in the catalytic cycle. Measures to prevent this problem are similar to those used in the Heck reaction. Transarylation can also be caused by the

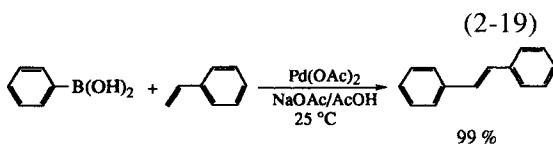


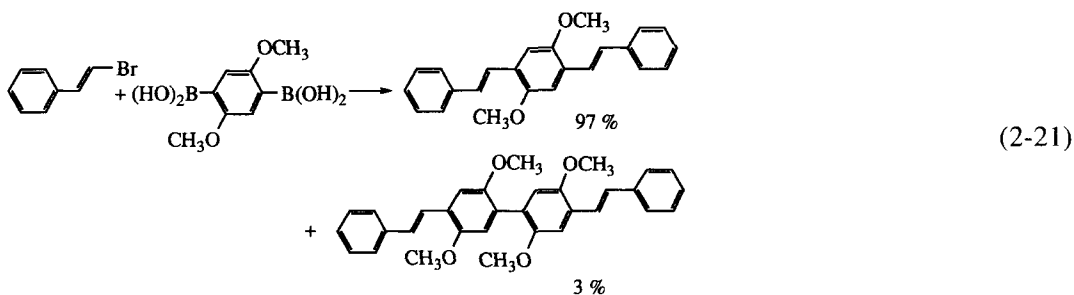
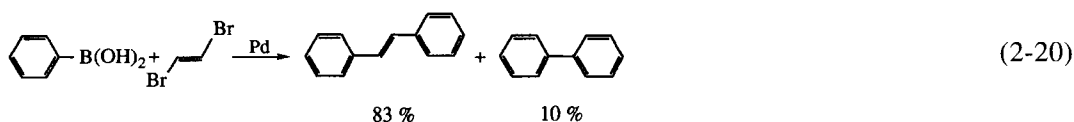
Scheme 2-3.

arylboronic acid. Similar to the homo coupling of the Grignard reaction in the presence of 1,4-dichloro-2-butene (Cheng, 1988), the homo coupling of organoboroxine results in high yields of the biaryl compounds in the presence of *o*-di(bromomethyl)benzene (Song and Wong 1994) (Eq. 2-18).



Obviously, oxidative addition of the furyl boronic acid to Pd(0) is involved in the catalytic cycle. Evidence for the oxidative addition of arylboronic acid is also given in the reaction of PhB(OH)<sub>2</sub> with styrene to *trans*-stilbene [Cho and Uemura (1994), Eq. 2-19]. This reaction works with high

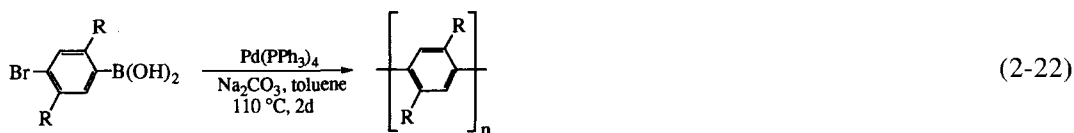




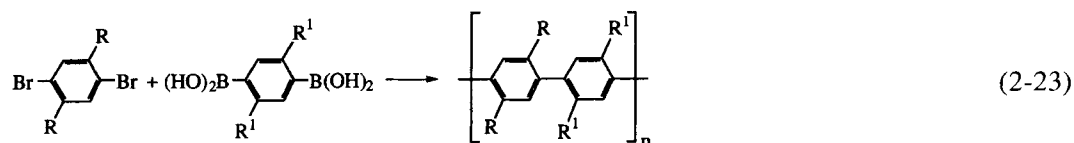
yields in acetic acid. Under the same conditions, ArJ gives only 7% stilbene. Many solvents other than acetic acid, such as DMF or benzene, are ineffective in this reaction, the yield of stilbene being lower (14–16%) with biphenyl (1–16%) formed as a side product. A mechanistic study showed that the self-coupling of arylboronic acid is not negligible, if the Suzuki reaction is slow, i.e., when electron-donating substituents are present (Moreno-Mañas et al., 1996). No biaryl coupling was observed with dba as the ligand. Biaryl formation is also observed in the reaction of phenylboronic acid with *trans*-1,2-dibromoethylene (Koch and Heitz, 1992). It is

lower for oligomers (Eq. 2-21) and polymers.

In particular, the synthesis of a variety of substituted poly-*p*-phenylenes was accomplished by the Suzuki reaction. Well-defined structures are obtained as a result of the regiospecificity of this reaction (Rehahn et al., 1989b). The solubility is increased by substituents (Rehahn et al., 1990a; Rau and Rehahn, 1993; Huber and Scherf, 1994; Hu et al., 1996a, b; Eq. 2-22). Alternating copolymers (Rau and Rehahn, 1993; Witteler et al., 1993; Eq. 2-23) and ansa-polyphenylenes (Eq. 2-24) with a random configuration were also obtained via the Suzuki route (Huber and Scherf, 1994).



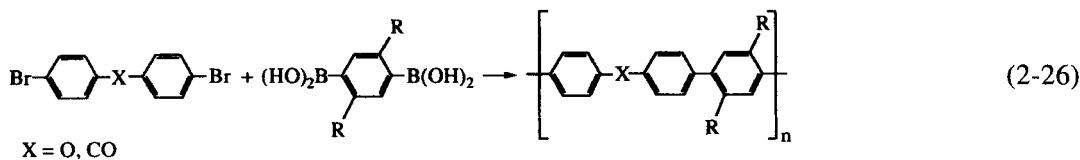
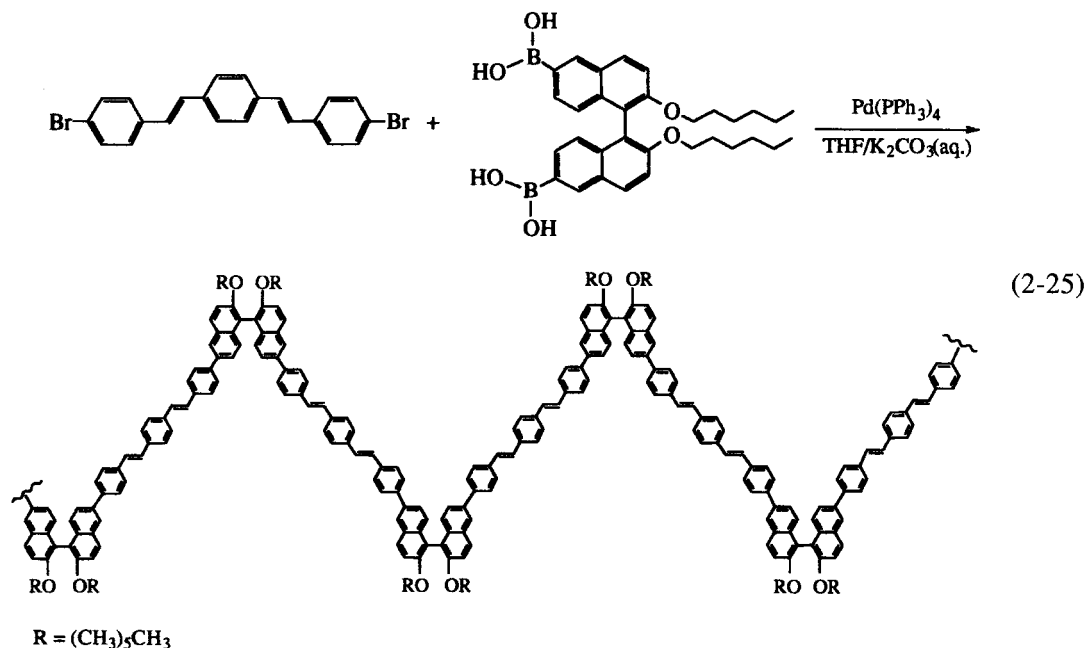
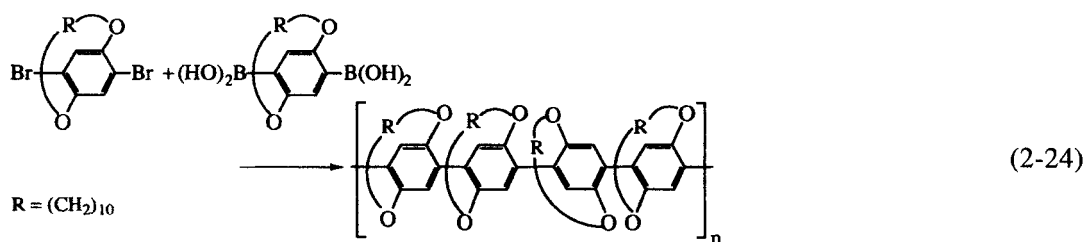
R = CH<sub>3</sub>, CH<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>, (CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub> (n = 3, 5, 6, 7, 8, 11, 15), CH<sub>2</sub>O(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>



R = C<sub>6</sub>H<sub>13</sub>, C<sub>12</sub>H<sub>25</sub>, (CH<sub>2</sub>)<sub>3</sub>C<sub>6</sub>F<sub>13</sub>, (CH<sub>2</sub>)<sub>3</sub>C<sub>6</sub>F<sub>17</sub>, CH<sub>2</sub>O(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>

R' = C<sub>6</sub>H<sub>13</sub>, C<sub>12</sub>H<sub>25</sub>

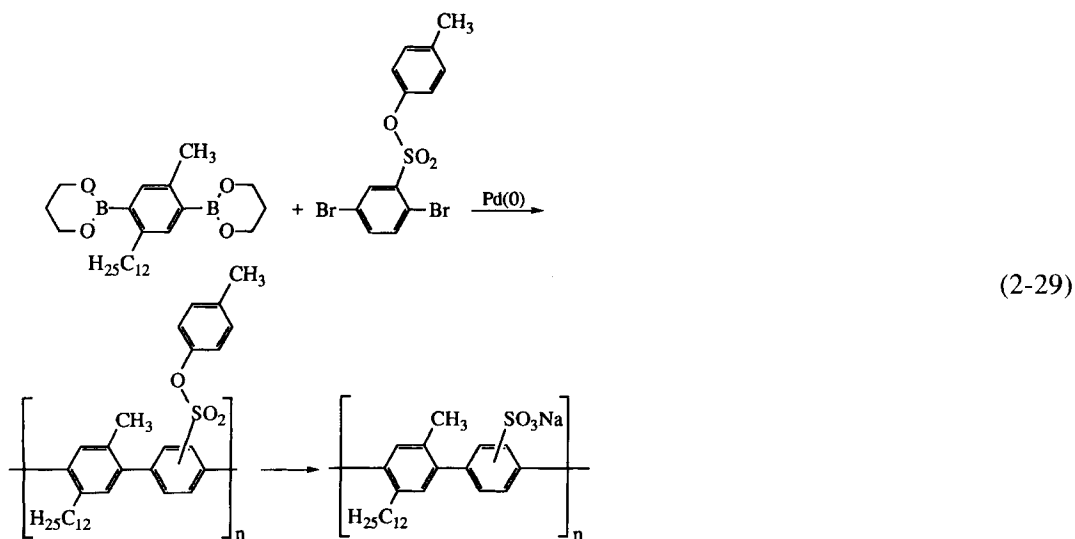
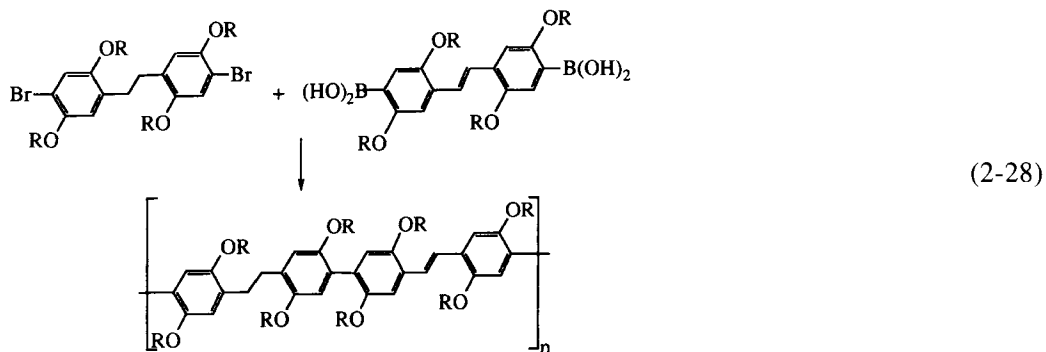
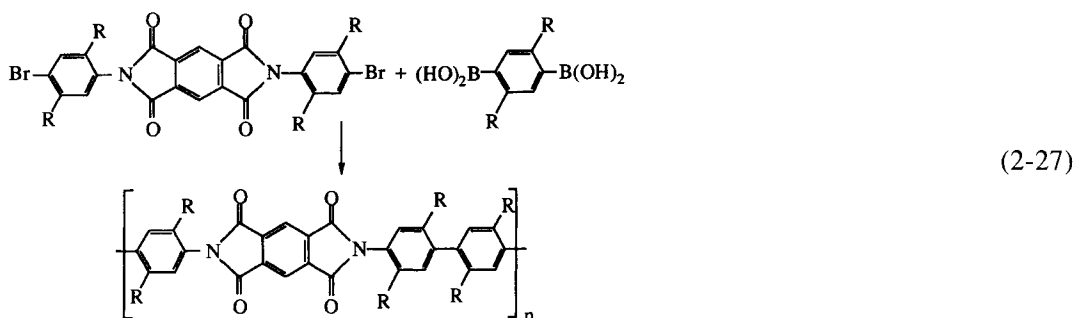




Poly(arylene vinylene)s with main chain chiral configurations were obtained by the Suzuki route, and the chirality was demonstrated by the CD spectrum [Hu et al., (1996 a, b), Eq. 2-25].

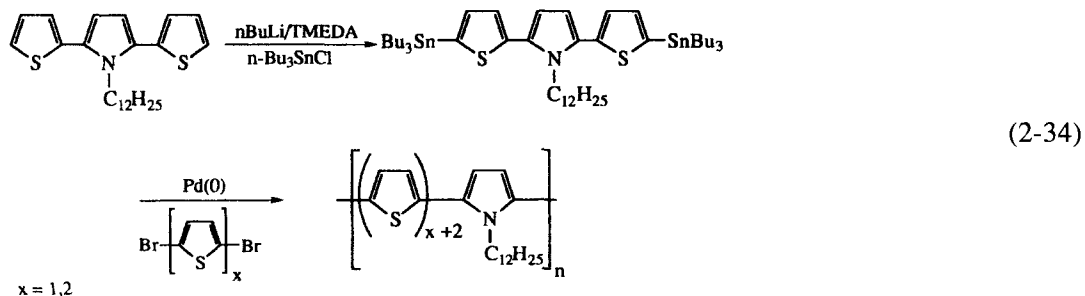
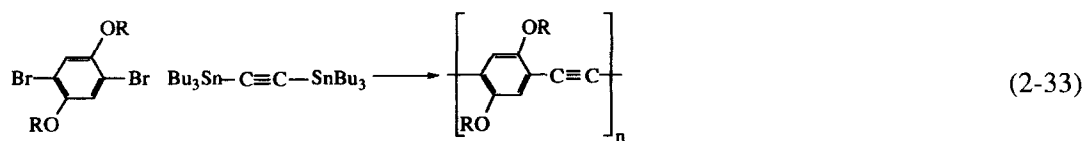
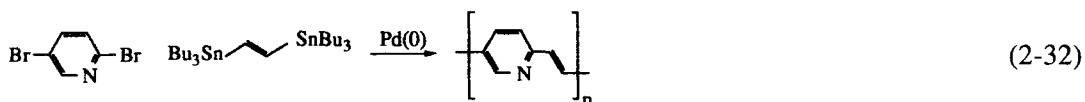
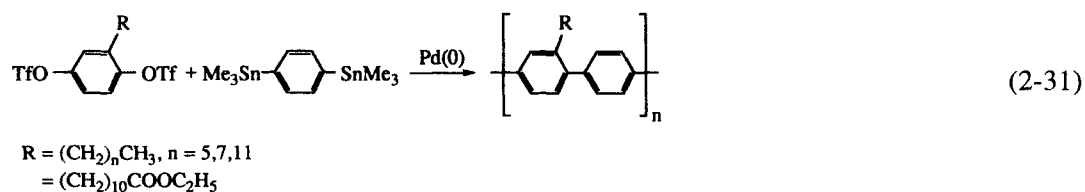
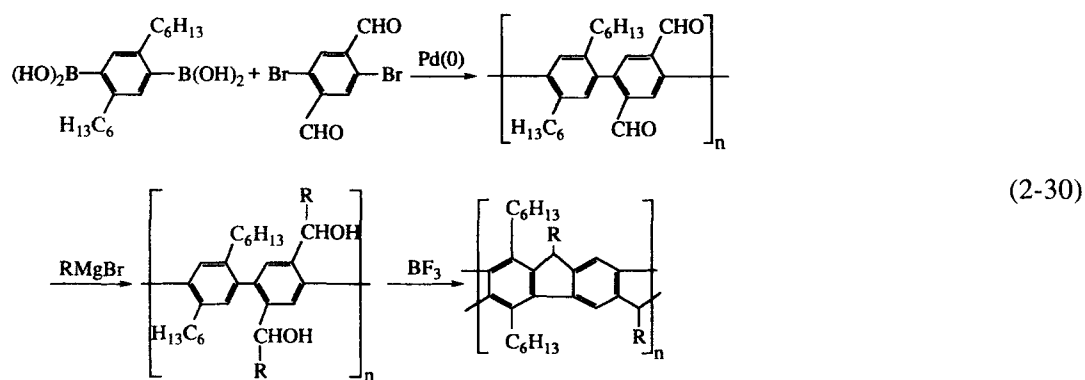
A variety of groups can be part of the polymer chain. Ether-, keto-, and imide-containing polymers were thus obtained (Rehahn et al., 1990b; Helmer-Metzmann et al., 1992; Eq. 2-26 and 2-27).

It is possible to tune the photo- and electroluminescence by combining conjugated with nonconjugated monomers (Remmers et al., 1996; Eq. 2-28). Rod-like polyelectrolytes were synthesized starting with carboxylic acid (Wallow and Novak, 1991) or the sulfonate [Rulkens et al. (1994), Schild and Reynolds (1994), Eq. 2-29].



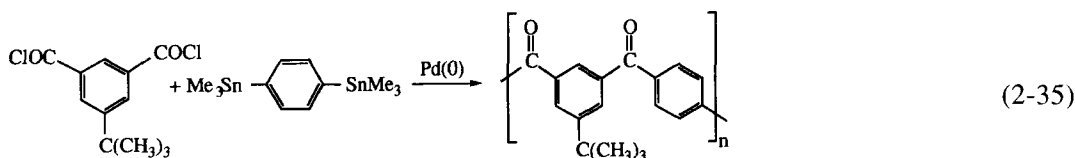
Well-defined ladder-type polymers with a variety of structures were prepared with the key step being the Suzuki reaction (Scherf and Müllen, 1991, 1992 a, b; Eq. 2-30).

Again, the synthesis makes use of the tolerance of palladium-catalyzed reactions towards functional groups.



The Stille reaction allows a similar range of structures to be synthesized. Examples of poly(phenylenes) (Quian and Pena, 1995; Eq. 2-31), poly(phenylene vinylene)s (Marsella et al., 1995b; Eq. 2-32), and poly(phenylene acetylene)s (Yu et al., 1993; Eq. 2-33) are

described. Many polymers with thiophene units were obtained using the Stille reaction (Yu et al., 1993; Parakka et al., 1996; Marsella and Swager, 1993; Marsella et al., 1995c; Eq. 2-34). Polythiophenes are of growing interest due to their electrical and



transport properties, which make them useful for polymeric LEDs and sensors. Starting with acyl chloride, polyketones are available (Moore and Decter, 1991; Eq. 2-35).

### 2.2.1.3 Removing X<sub>2</sub>

Nickel-catalyzed reduction coupling of aryl halides has been widely used to produce aromatic main chain polymers. This reaction, described by Kumada (Tamao et al., 1972; Eq. 2-36), was first used by Yamamoto et al. (1978, 1985)



to synthesize poly-*p*-phenylene. As a result of the insolubility of the material, the polymer precipitates at low molecular weights. X can be halide (Tamao et al., 1976), triflate (Sengupta et al., 1992), and mesylate (Per-

cec et al., 1996a). Reducing agents are lithium (Marakashi et al., 1979), magnesium (Tamao et al., 1972), and zinc (Knochel and Singer, 1993). Nickel- and palladium-mediated electrochemical reduction to polypyridine is also described (Yamamoto and Saito, 1996). As catalyst, the use of nickel is favored, but palladium (Kunada, 1980), silver and iron (Tamura and Kochi, 1971) can be used as well. NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and Ni(0) compounds are commonly applied catalysts precursors. However, in the catalytic cycle, Ni(I/III) species are involved (Kochi, 1980; Anton et al., 1984; Eq. 2-37–2-39).

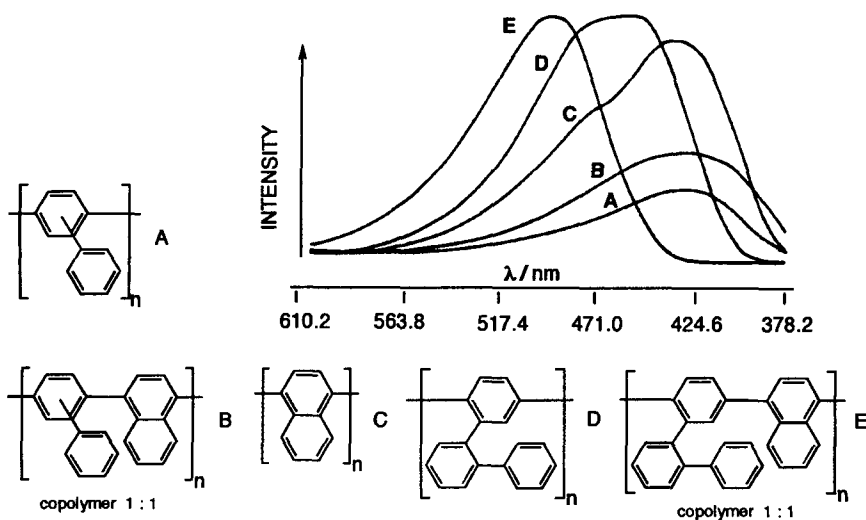
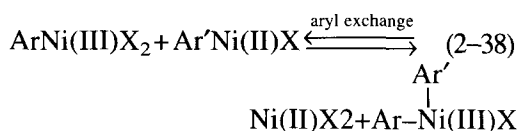
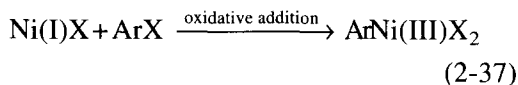
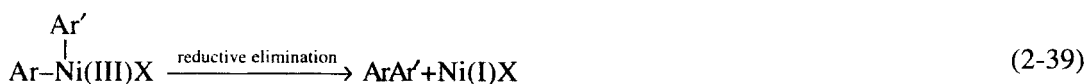


Figure 2-5. Photoluminescence spectra of different PPPs.

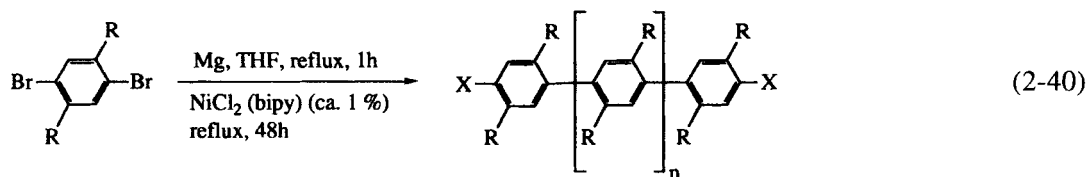


A variety of polyphenylenes have been synthesized this way [Rehahn et al. (1989 a), Eq. 2-40; Noll et al. (1990), Eq. 2-41; Goldfinger and Swager (1993), Eq. 2-42], mainly to tune the solubility and the optical properties [Heitz (1995), Fig. 2-5].

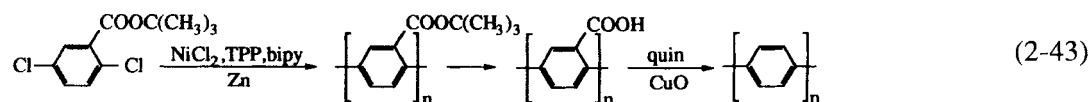
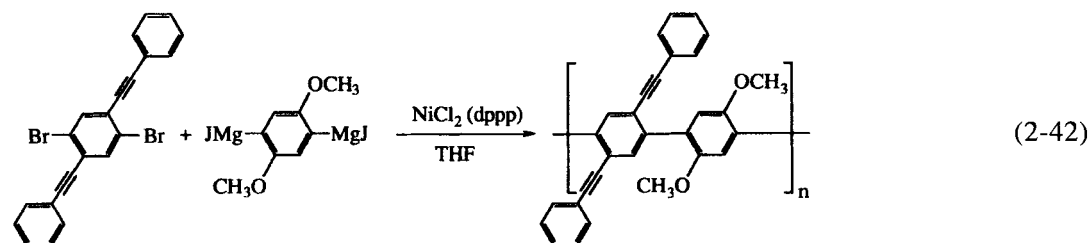
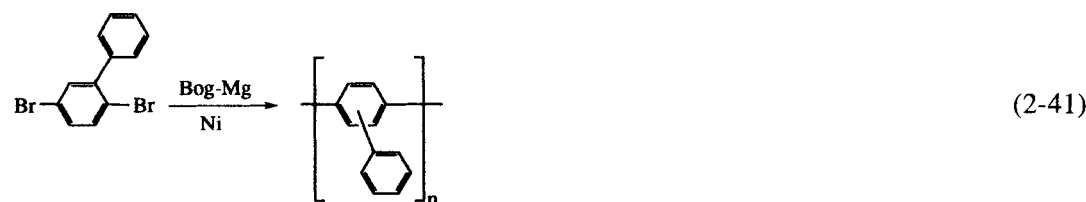
In order to obtain high molecular weight-material, activated magnesium (Bogdanovic et al., 1988; Rieke 1989) should be used. The procedures described by Bogdanovic et al. (1988) and Rieke (1989) are adequate. Otherwise, polymers of lower molecular

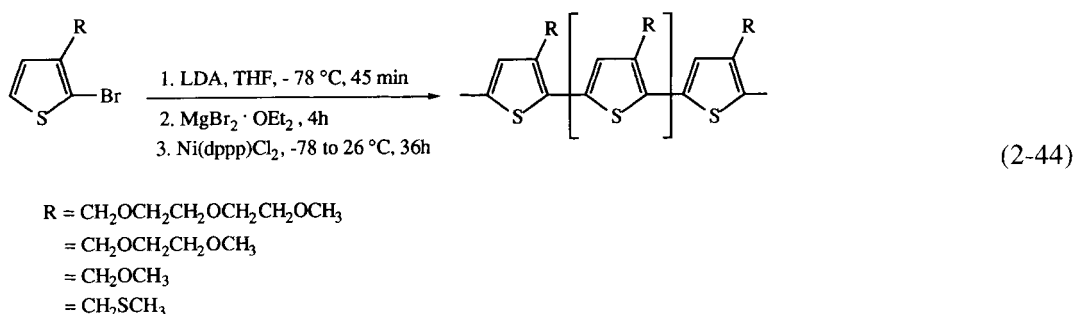
weight with the corresponding high bromine content are obtained. PPP with ester groups was obtained using zinc as the reducing agent [Ueda and Yoneda (1995), Eq. 2-43]. This soluble PPP was saponified and decarboxylated.

Polythiophenes with alkyl, alkylether, alkylthioether, and phenyl substituents were prepared using magnesium [McCullough and Williams (1993), Eq. 2-44] or zinc (Chen et al., 1993; Ueda et al., 1991). Regioregular substitution is important for



$r = \text{hexyl, n-octyl}$





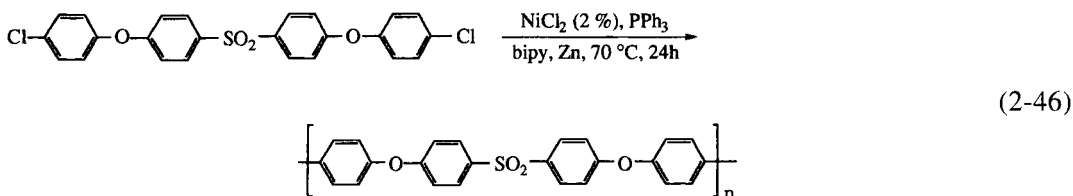
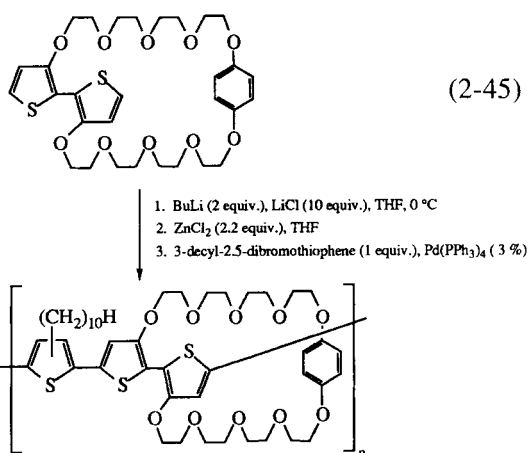
electroconductive polymers. The influence of the reaction conditions on the control of regioselectivity has been studied in detail (McCullough and Williams, 1993; Chen and Rieke, 1992; Chen et al., 1995). Regioregular and regioirregular PPPs have been obtained in a nickel-catalyzed homo coupling with mesylate as the leaving group (Percec et al., 1996b). The nickel/zinc route was also used to prepare PPP containing

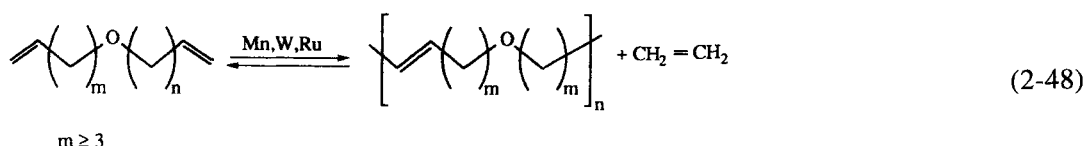
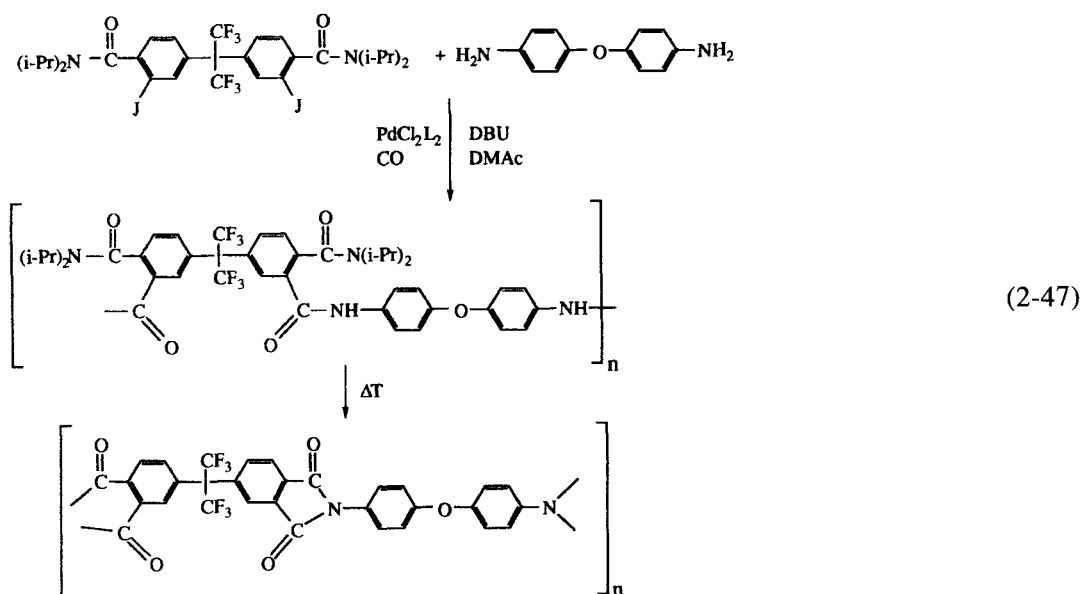


as a substituent with second order NLO behavior (Wright and Toplikar, 1995). A polythiophene with crown ether substituents showed reversible changes of the electroconductivity [Marsella et al. (1994), Eq. 2-45]. A property that can be used to construct sensors.

The synthesis of polyethersulfones with high inherent viscosities ( $\eta_{\text{inh}} = 0.81 \text{ dl/g}$ ) was accomplished by the nickel-catalyzed reductive coupling of chloroarenes with zinc [Cotan and Kwiatowski (1990), Ueda and Ito (1991), Eq. 2-46]. Poly(ether ketone)s prepared in the same way have a mo-

lecular weight limited by the solubility of the crystalline polymer (Ueda and Ichikawa, 1990). Polyimides were obtained in a palladium-catalyzed reaction by the carbonylation of diiodoesters with diamines (Perry et al., 1995a, b). However, a soluble, hydrolytically stable precursor was not obtained. Going through a poly(amic amide) intermediate, ring closure can be delayed to the final thermal treatment [Perry et al. (1996), Eq. 2-47].





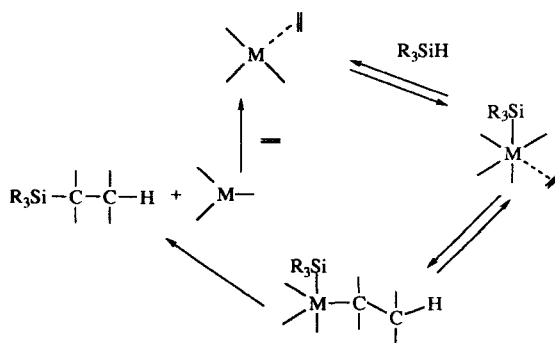
The acyclic diene metathesis polymerization is a polycondensation with a metathesis reaction as the chain-growing step (Brzezinska et al., 1996). By removing the ethylene, the equilibrium is shifted towards polymer formation (Eq. 2-48). Typical metathesis catalysts can be used (Schwab et al., 1995; Schrock et al. 1990).

plausible mechanism can be formulated (Scheme 2-4). Oxidative addition of silicon hydrides is presumed to be an obligatory step in catalytic hydrosilylation. It is uncertain whether the olefin is coordinated prior to the oxidative addition step. Relative rates of ethylene hydrosilylation have been compared for three catalysts (Collman et al.,

## 2.3 Polyaddition Reactions

### 2.3.1 SiH Addition to Carbon Double Bonds

The metal-catalyzed addition of the silicon-hydrogen bond to a carbon-carbon multiple bond, termed hydrosilylation, is an excellent method of preparing silicon-carbon bonds (Collman et al., 1987; Speier, 1979). On the basis of product analysis, a

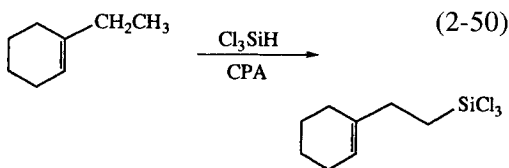
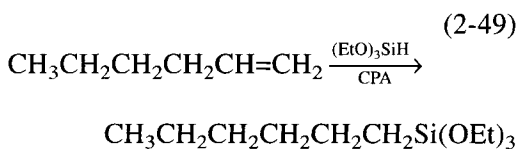


Scheme 2-4.

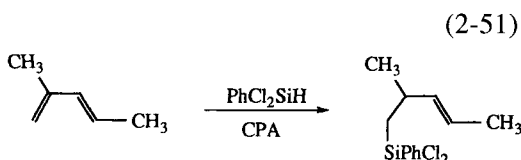
1987); however, such comparisons depend upon the nature of the olefin and silane.



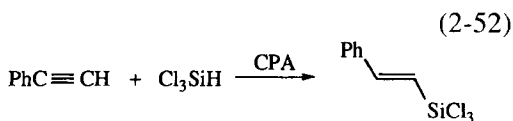
The most commonly used catalyst for hydrosilylations is chloroplatinic acid (CPA). It has the advantages of being effective at very low concentrations ( $10^{-5}$  M or even less in certain cases), the avoidance of excessive heat to carry out the reaction, and the ability to carry out the reaction in the absence of solvent. It is also very tolerant of a range of organic functionalities, including nitro, cyano, ester, amino, sulfonic esters, borate esters and even phosphine oxides, among others. Hydrosilylation with CPA occurs regioselectively to place the silicon on the terminal carbon (Eq. 2-49). The reaction does not proceed well with internal olefins, in which case olefin isomerization is often observed (Eq. 2-50).



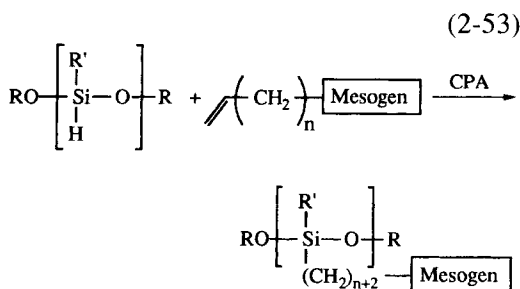
Terminal double bonds react preferentially over internal double bonds, as evidenced from the hydrosilylation of dienes (Eq. 2-51).



The hydrosilylation of alkynes is also possible with the addition being predominantly cis (Eq. 2-52). Alkynes are more reactive than olefins.



Several examples of grafting reactions involving SiH-containing poly(dimethyl siloxane)s are based upon hydrosilylation (Ilgr et al., 1980). This reaction is a key step in the synthesis of many LC side chain polymers [Finkelmann (1987), Eq. 2-53] and the crosslinking reaction in many dental medical applications.

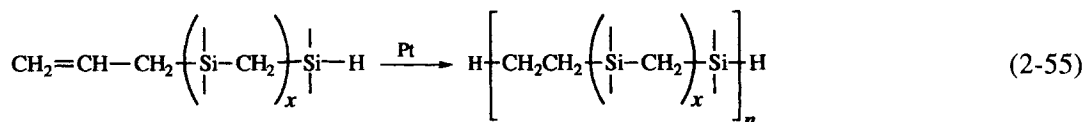
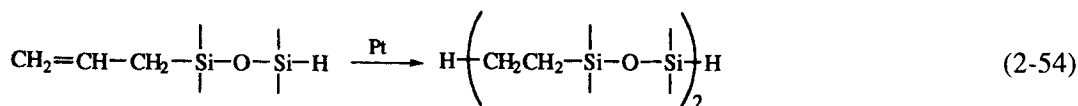


$\alpha$ -Hydro- $\omega$ -alkyl-oligo(dimethyl siloxane) [Greber and Metzinger (1960), Eq. 2-54] and 1-hydro-3-vinylsilmethylene [Greber and Degler (1962), Eq. 2-55] underwent selfcondensation.

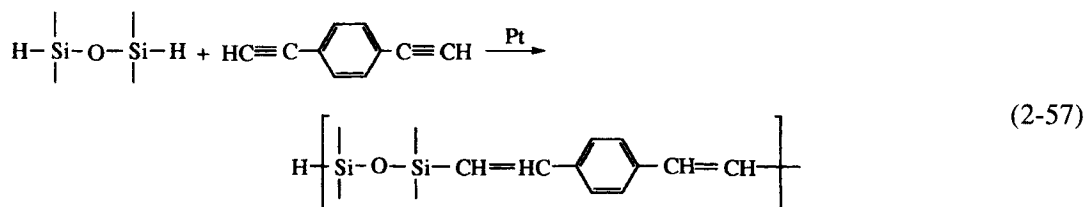
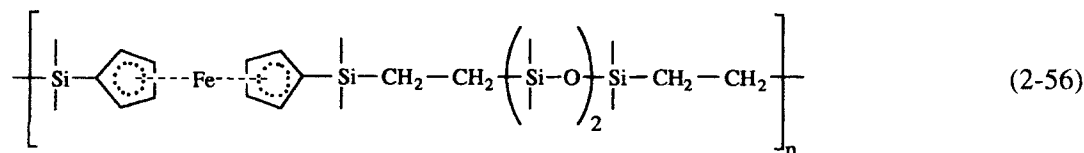
Starting from a ferrocene containing disilane and a divinylsiloxane, an elastomer was obtained with a higher thermal stability than poly(methylphenyl siloxane) [Greber (1968), Eq. 2-56].

Diacetylene monomer can be hydrosilylated as well (Lebedev et al., 1978; Andrianov and Zavin, 1972; Eq. 2-57). Obviously no dihydrosilylation of the triple bond occurs.





where  $x=1-3$

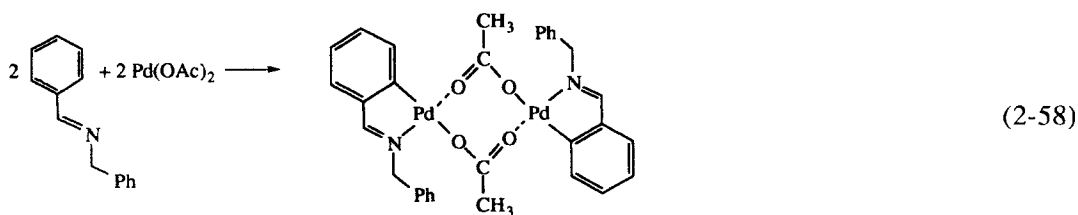


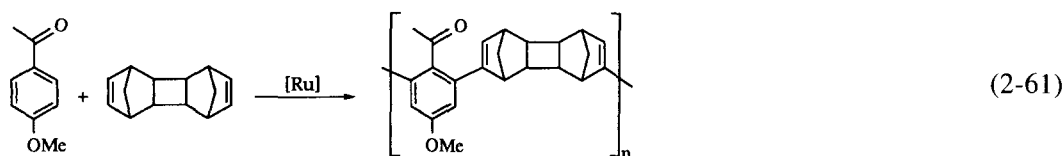
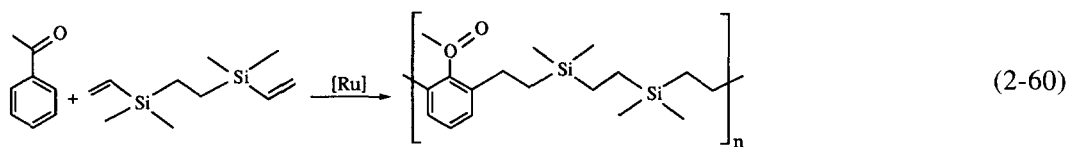
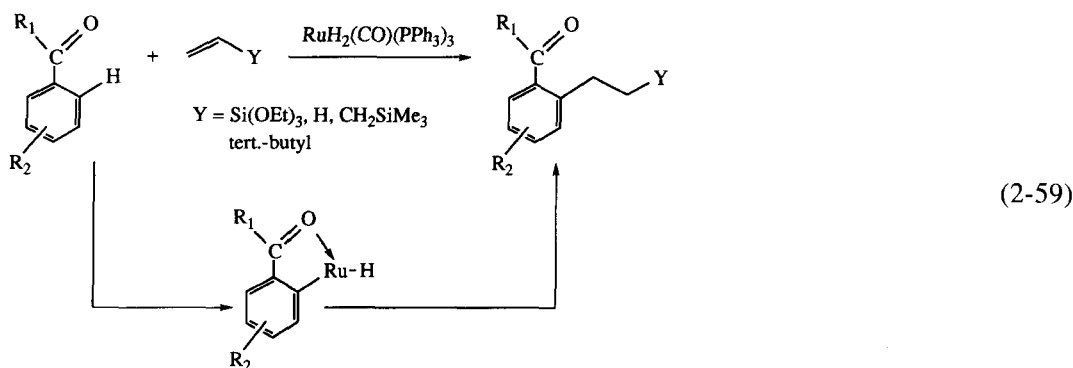
### 2.3.2 ArH Addition to Carbon Double Bonds

The direct and selective activation of ArH bonds has been known for many years in stoichiometric reactions (Collman et al., 1987). The addition of hydrogen in the ortho position to azomethine as opposed to carbonyl groups is a reaction with high selectivity [Heck (1987), Eq. 2-58].

Murai (Murai et al., 1993, 1994; Kakiuchi et al., 1995) uses this possibility in a catalytic fashion, which allows the addition of olefins.

Dihydridocarbonyltris(triphenyl phosphine) ruthenium  $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_2]$  catalyzes the cleavage of ortho C–H bonds of acetophenone and the subsequent addition of the C=C of the olefins to yield ortho alkyl substituted acetophenone [Murai et al. (1993), Eq. 2-59].

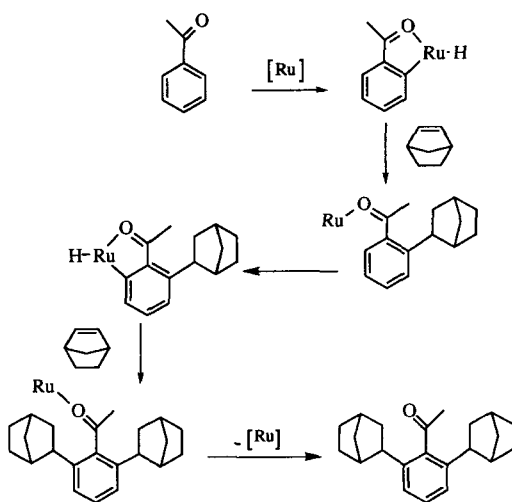




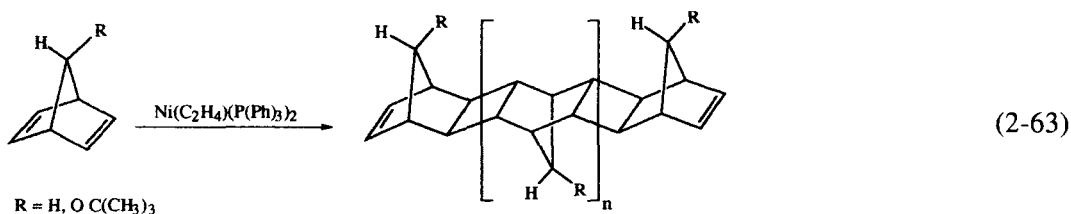
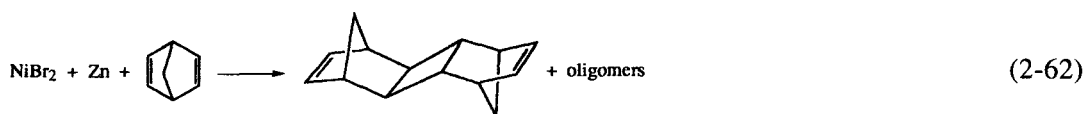
It is not known if the olefin is inserted into the Ar–Ru or Ru–H bond before reductive elimination takes place. With  $\text{CH}_2=\text{CH}-\text{Si}(\text{OEt})_3$ , the regioselectivity (1,2-addition versus 1,1-addition) is 99:1, whereas it is only 84:16 with styrene.  $\alpha$ -Olefins show a strong tendency to double bond migration. Norbornene reacts exclusively to the *exo* addition product, similar to the behavior in palladium-catalyzed reactions (Percec and Hill, 1996; Arcadi et al., 1989; Brunner and Krammler, 1991).

The reactivity of the second ortho position is much lower than that of the first. This results in long reaction times if disubstitution or polyaddition is aimed at. The ratio of di- to monosubstitution is influenced by the olefin. Norbornene is an exception. This is most probably due to a steric requirement in the catalytic cycle which brings the coordinated ruthenium in proximity to the sec-

ond ortho position [Bhattacharjee and Heitz (1996), Scheme 2-5]. Electron-donating substituents ( $\text{R}_2$ ) enhance the reaction. A variety of polymers have been obtained by



Scheme 2-5.

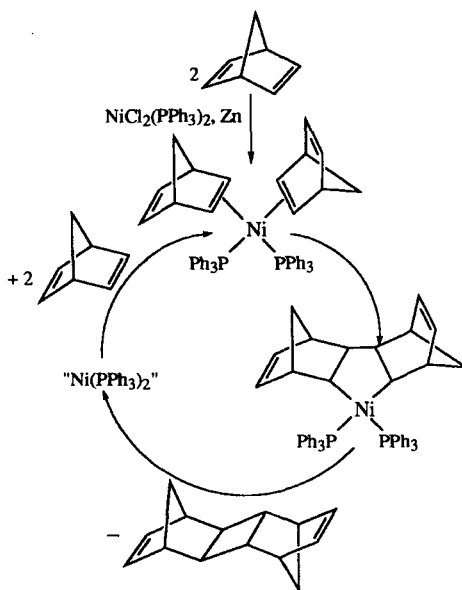


this ruthenium-catalyzed reaction [Guo and Weber (1994, 1995), Guo et al. (1994, 1995a, b, c), Eq. 2-60, Bhattacharjee and Heitz (1996), Eq. 2-61].

### 2.3.3 Cycloaddition Reactions

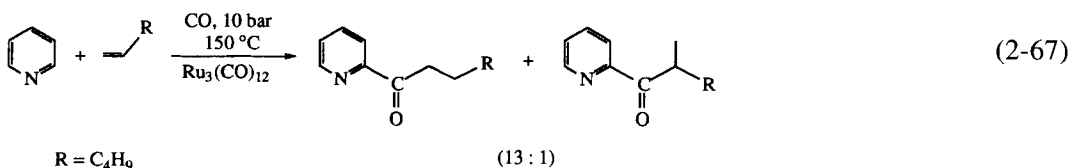
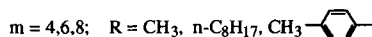
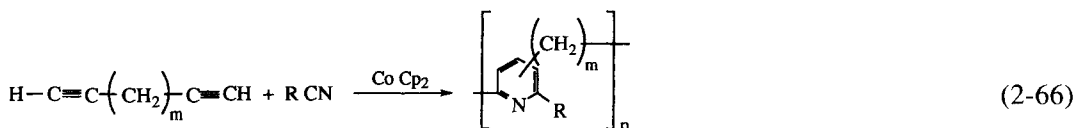
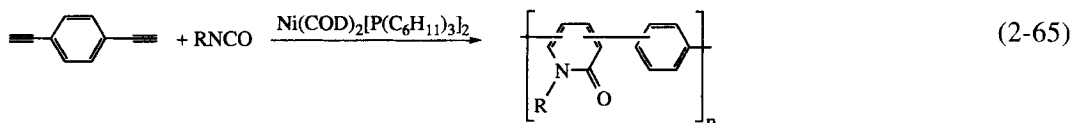
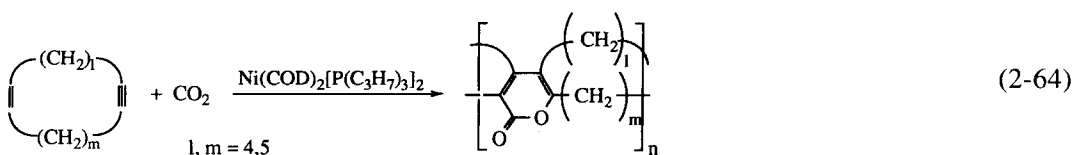
While ruthenium catalyzes only the [2+2]-cycloaddition of alkynes with norbornene as opposed to norbornadiene (Mitsudo et al., 1994), Ni(0) can catalyze the [2+2]-cycloaddition of norbornadiene [Huang and Cheng (1995), Eq. 2-62].

The catalytic species are reacted in situ with norbornene. The *exo-trans-exo* dimer can be obtained in high yields by sublimation. The reaction is enhanced in the presence of two equivalents of  $\text{PPh}_3$  as the ligand. If the reaction is run stoichiometrically, the catalytic species can be precipitated by ethanol. The catalyst is stable against water, but air-sensitive. The approximate composition is  $\text{Ni}(\text{C}_7\text{H}_8)(\text{PPh}_3)_2$ . The ethylene complex  $\text{Ni}(\text{C}_2\text{H}_4)(\text{PPh}_3)_3$  is a well-defined catalyst giving the same reaction [Herth and Heitz (1998), Scheme 2-6]. A proposal for the catalytic cycle includes a metalacyclopentane. The stereochemistry is influenced by the ligand. With the ligand-free catalyst, the dimer is formed in an *exo-trans-exo* to *exo-trans-endo* ratio of 92:8. Phosphine-containing catalysts produce both isomers



Scheme 2-6.

in nearly equal amounts, which can be isolated and identified after short reaction times. With longer reaction times, polymers are formed. Both chain ends contain one double bond, as shown by NMR. With  $\text{R} = \text{H}$ , the limit of solubility is at around  $M = 4000$ ; with  $\text{R} = 0$ -*tert*-butyl, the polymer is soluble with a molecular weight of 7000. As a result of the fact that *exo-endo* units should be statistically present, the molecule is expected to have the shape of a two-dimensional coil. It belongs to the class of polymers



coined 'single chain glasses' by de Gennes (1979).

Nickel catalyzed the [2+2+2]-cycloaddition of diacetylene with carbon dioxide [Tsuda et al. (1985 a, b), Eq. 2-64] or isocyanates [Tsuda and Tobisawa (1995), Eq. 2-65] to form poly(2-pyrone)s. A possible side reaction is the trimerization of acetylene groups.

Commercially available cobaltocene catalyzes the reaction of aliphatic terminal alkynes with a nitrile [Tsuda and Machara (1996), Eq. 2-66].

There are a variety of catalytic addition reactions that have not yet been explored for polymer synthesis. Examples are the ruthenium-catalyzed formation of pyridine ketones [Moore et al. (1992), Eq. 2-67], or the ytterbium or yttrium-catalyzed synthesis of quinoline derivatives (Makioka et al., 1995).

## 2.4 References

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## 3 Ring-Opening Metathesis Polymerization (ROMP) and Related Processes

Robert H. Grubbs and Ezat Khosravi

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## List of Symbols and Abbreviations

$F_D$	Figure of merit
$h$	Planck's constant
$k_i$	rate of initiation
$k_p$	rate of propagation
$k_{als}$	anti to syn rate constant
$k_{sta}$	syn to anti rate constant
$m$	number
$M_n$	number average molecular weight
$M_w$	weight average molecular weight
$n$	number
$T_g$	glass transition temperature
$x$	average chain length
$\epsilon_R$	relaxed dielectric constant
$\epsilon_u$	permittivity
$\nu$	frequency
Ac	acetyl
BTFMND	bis(trifluoromethyl)norbornadiene
Bu	butyl
COT	cyclooctatetraene
Cp	cyclopentadienyl
Cy	cyclohexyl
DCNBD	5,6-dicarbomethoxynorbornadiene
DP	degree of polymerization
DSC	differential scanning calorimetry
Et	ethyl
GPC	gel permeation chromatography
LC	liquid crystalline
M	metal
Me	methyl
MTD	methyltetracyclododecene
NMR	nuclear magnetic resonance
PDI	polydispersity
Ph	phenyl
PL	photoluminescence
PMMA	poly(methylmethacrylate)
PPV	poly(3,4-diisopropylidenecyclobutene)
Pr	propyl
PROMP	photoinitiated ROMP
PVDF	poly(vinylidene fluoroide)
py	pyridine
RCM	ring-dosing metathesis

ROM	ring-opening metathesis
ROMP	ring-opening metathesis polymerization
SAXS	small-angle X-ray scattering
SCLCP	side chain liquid crystalline polymer
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
THF	tetrahydrofuran
$t_{os}$	<i>p</i> -toluenesulfonate
TSC	thermally stimulated current
WAXS	wide-angle X-ray scattering

### 3.1 Introduction

Over the last 15 years, metathesis initiators have evolved from the poorly defined, heterogeneous mixtures that characterized early systems to well-defined, single component metallacycles and alkylidenes.

The ill-defined initiators suffer from many disadvantages. Of primary significance is the fact that such initiating systems are ill-defined; in other words the precise nature of the active site at the metal center is not known, and species with other catalytic activities are formed. In addition, the metal carbene must be generated before initiation and subsequent propagation can commence. This process usually proceeds with very low yield, and the activity of a given initiating system is dependent upon its chemical, thermal, and mechanical history, and upon the order and the rate of mixing of the catalyst, the cocatalyst, and the monomer. Since the propagation rates of these catalysts are very high, the slow initiation rates result in very poor control of the molecular weight distribution in the final polymers.

In contrast, the well-defined initiators react in controlled, predictable ways, and their activities can be fine-tuned through simple ligand substitution. Moreover, several of these well-defined alkylidenes initiate living ring-opening metathesis polymerization (ROMP). Historically, metathesis was limited to the polymerization of cyclic hydrocarbons in highly purified organic solvents due to the extreme sensitivities of early transition metal catalyst systems to

oxygen, water, and polar groups. The development of metathesis initiators, which are particularly tolerant of polar functional groups and protic solvents, offers several advantages, the most obvious being the use of substrates and solvent without rigorous purification and drying.

In this chapter we illustrate recent advances in the development of ROMP initiators. We hope to show that the development of more tolerant catalysts has resulted in broadening the scope of the metathesis reaction, enabling the well-controlled ROMP of highly functionalized monomers.

### 3.2 Development of Well-Defined ROMP Initiators

The first example of a well-defined carbene complex (**I**, Fig. 3-1), in which olefin metathesis could be observed via NMR, was reported in 1979 by Tebbe et al. The first well-documented example of the living ROMP of a cycloalkene was the polymerization of norbornene with the related titanacyclobutane complexes (**II**, **III**, Fig. 3-1) (Gillion and Grubbs, 1986; Grubbs and Thomas, 1989).

The metallacyclobutane exists in equilibrium with its ring-opened carbene form, which polymerizes the bicyclic olefin in a living manner, as shown in Scheme 3-1. In order to terminate the chain propagation, the metal site can be capped by adding a ketone (typically benzophenone) or an aldehyde. This class of initiator has been exploited to produce diblock and triblock copolymers of

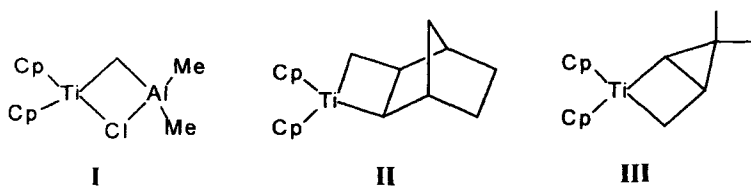
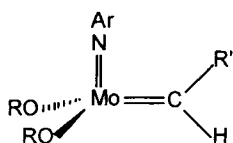
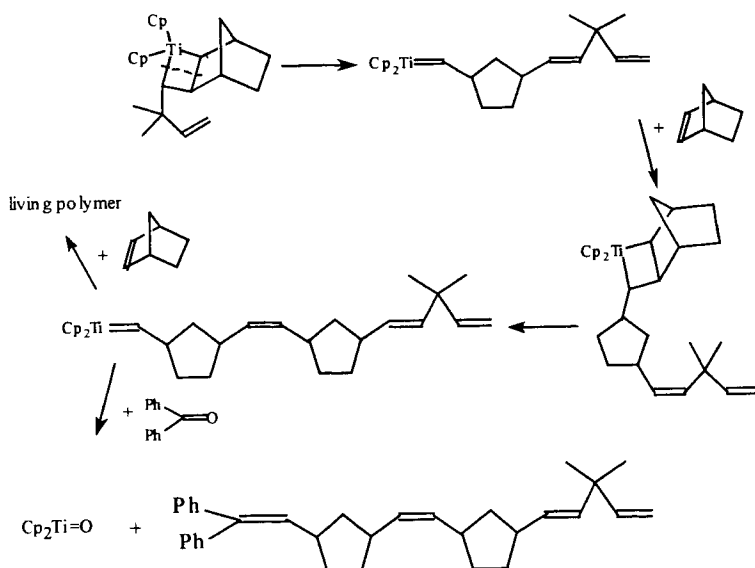


Figure 3-1.



M=Mo, W  
 Ar=2,6-C<sub>6</sub>H<sub>3</sub>i-Pr<sub>2</sub>  
 R=CMe<sub>3</sub>, CMe<sub>2</sub>Ph  
 OR'=OCMe<sub>3</sub>, OCMe<sub>2</sub>CF<sub>3</sub>, OCMe(CF<sub>3</sub>)<sub>2</sub>

Figure 3-2.

norbornene, substituted norbornenes, and dicyclopentadiene (Cannizzo and Grubbs, 1987, 1988). However, there are some drawbacks associated with this initiator system. Titanacyclobutanes require temperatures of 50 °C in order to ring-open norbornenes, and, moreover, they are very reactive towards functionalities owing to the highly electrophilic nature of the metal center. Therefore the range of suitable monomers is limited to relatively stable hydrocarbons.

The next important step was the preparation of the first well-characterized tungsten alkylidene complexes of the type W(CH-*t*-Bu)(OCH<sub>2</sub>-*t*-Bu)<sub>2</sub>X<sub>2</sub> (X=a halide) (Kress

et al., 1982, 1986; Kress and Osborn, 1983, 1987). These complexes require a Lewis acid cocatalyst for high activity, probably in order to generate four coordinate cationic species [W(CH-*t*-Bu)(OCH<sub>2</sub>-*t*-Bu)<sub>2</sub>X]<sup>+</sup>. Related complexes of the type W(CH-*t*-Bu)(OAr)<sub>2</sub>X<sub>2</sub> have been synthesized and used to metathesize olefins in the presence of alkyl tin reagents, but the exact nature of the active species in these cases has not been fully established (Quignard et al., 1986, 1987). The activity of W(CH-*t*-Bu)(OAr)<sub>2</sub>X<sub>2</sub> catalysts can be controlled to some extent by altering the nature of the OAr ligand, with more electron-withdrawing phenoxides giving more active catalysts.

Well-defined tungsten and molybdenum initiators with bulky alkoxide and arylimido ligands of the type M(CHR)(NAr)(OR')<sub>2</sub>, as shown in Fig. 3-2, only became synthetically available in the mid-1980s (Schrock et al., 1988 a, 1990).

The X-ray structure of W(NAr)(CH-*t*-Bu)(O-*t*-Bu)<sub>2</sub> shows that it is a pseudo tetrahedral species with the alkylidene substituent pointing towards the imido nitrogen

atom (*syn* rotamer). The linear triply bonded imido unit (W-N-C angle of  $169^\circ$ ) forces the  $\beta$ -carbon atom of the alkylidene unit to lie in the same plane as the nitrogen, tungsten, and  $\alpha$ -carbon atoms (Schrock et al., 1988 a). The tetrahedral coordination of these complexes allows relatively small substrates, such as olefins, to attack the metal to give five coordinate metallacyclobutane intermediates, while the bulky alkoxide and 2,6-di-isopropylphenylimido units help prevent decomposition.

The acyclic olefin metathesis activity of these complexes is controlled by varying the nature of the alkoxide group. Hexafluoro-*t*-butoxide catalysts are more active for metathesis of ordinary internal olefins, for which *t*-butoxide complexes are virtually inactive (Feldman and Schrock, 1991; Fox et al., 1992, 1993; Schaverien et al., 1986). This is because the interaction can be regarded as an electrophilic attack on the olefin by the metal, and the metal is significantly more electrophilic (and hence more reactive) with the electron-withdrawing fluorinated alkoxides present. This lower reactivity of the bis *t*-butoxide derivatives can be exploited in the polymerization of cyclic olefins, since both the molybdenum and tungsten complexes metathesize the strained double bond of norbornene to yield polymers, without reaction with the double bonds in the resulting polymer (backbiting) occurring. This gives the opportunity of preparing well-defined polymers in a controlled manner (Schrock, 1986, 1990 a, 1993; Bazan et al., 1989, 1990, 1991 a, b; Feast et al., 1992 a, b; Schrock et al., 1978,

1986, 1987, 1991; Toreki et al., 1992; Knoll et al., 1988; Knoll and Schrock, 1989; Schlund et al., 1989; Krouse and Schrock, 1988).

The molybdenum catalyst is less active than the tungsten analog, and molybdenum-acyclobutane complexes are much less stable than analogous tungstacyclobutane complexes towards the loss of olefins (Schrock et al., 1987; Knoll et al., 1988; Krouse and Schrock, 1988; Knoll and Schrock, 1989). Another important difference between tungsten and molybdenum, which correlates with their relative reactivities towards olefins, is that tungsten appears to be much more reactive towards functionalities. Such differences will be extremely important in polymerization reactions of cyclic olefins which have a functionality that is remote from the double bond undergoing reaction. As well as the *syn* rotamer shown in the crystal structure, the *anti* rotamer, where the alkylidene substituent points away from the imido nitrogen atom, is also possible (Fig. 3-3) (Feldman and Schrock, 1991; Schrock et al., 1978, 1991; Toreki et al., 1992; Schrock, 1986; Oskam and Schrock, 1992, 1993; Feast et al., 1994 a).

Rotamer interconversion rates have been measured for several members of the class of  $M(NR)(CHR')OR''$  complexes. The most extensive study involved molybdenum complexes in which  $OR''$  is a phenoxide (Schrock et al., 1991). Such studies were possible because both rotamers could be observed, and therefore standard  $^1H$  NMR techniques could be employed in order to determine rate constants and activation pa-

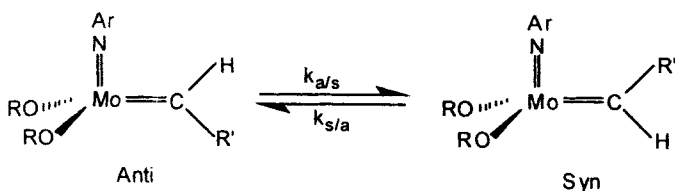


Figure 3-3.

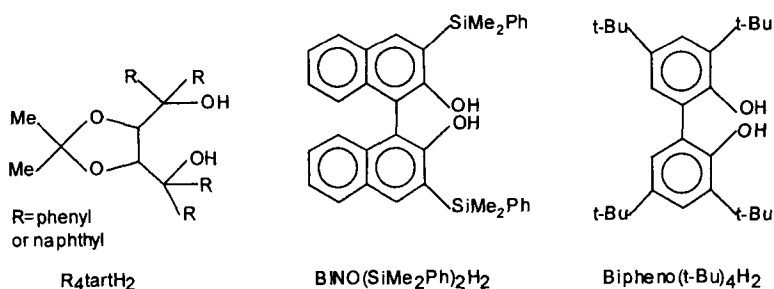


Figure 3-4.

rameters. The rate of rotamer isomerization in toluene-*d*<sub>8</sub> slows dramatically as the alkoxide ligands become more electron-withdrawing. The rate of conversion of the *anti* to the *syn* rotamer in toluene is found to vary by at least five orders of magnitude as the alkoxide is changed from *t*-butoxide to OC(CF<sub>3</sub>)<sub>2</sub>(CF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>). Addition of bis(trifluoromethyl) norbornadiene (BTFMND) to mixtures containing both *anti* and *syn* Mo(CHCMe<sub>2</sub>Ph)(NAr)[OCMe(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub> showed that the *anti* rotamer was orders of magnitude more reactive than the *syn* rotamer. It is clear that the polymerization pathway could dramatically depend upon the conditions, the nature of the alkoxide, and the inherent reactivity of the monomer, and that reactions could proceed entirely via the minor, virtually unobservable *anti* rotamer, if *syn/anti* interconversion is fast relative to the rate of polymerization, or entirely via the major *syn* rotamer, if *syn/anti* interconversion is slow relative to the rate of polymerization. The results of polymerizations (40–100 equiv. of BTFMND) at 25 °C suggests a relationship between alkylidene rotamer isomerization rates and polymer *cis/trans* content when the initiator contains an arylimido ligand; high-*cis* polymers are formed when rotamer isomerization rates are negligible on the time scale of polymerization, while high-*trans* polymers are obtained when rotamer isomerization rates are fast on the time scale of polymerization.

Controlling the stereochemistry of polymers prepared by the ring-opening of norbornenes and norbornadienes has been a topic of long-standing interest (Ivin, 1983; Draughton et al., 1985), one that could ultimately be solved by employing well-characterized chiral catalysts with known structures and activities. A chiral catalyst might be prepared by using chiral diolates (tartarate derivatives, binaphtholates, etc.) or a chiral imido ligand. Catalysts of the type Mo(CH-*t*-Bu)(NAr)OR)<sub>2</sub> have been shown to ring-open polymerize BTFMND to give highly tactic all-*trans* poly(BTFMND) when OR=O-*t*-Bu (in toluene or THF) (Bazan et al., 1990), and all-*cis* poly(BTFMND) with a *tactic* bias of ~74% when OR=OCMeCF<sub>3</sub>)<sub>2</sub> (in THF) (Feast et al., 1992 a). It has been shown that chiral catalysts of this general type can be prepared that contain the C<sub>2</sub>-symmetric chiral diolate ligands, as shown in Fig. 3-4, and that poly(BTFMND) and related polymers can be prepared using chiral catalysts that are >99% *cis* and >99% *tactic* (McConville et al., 1994; O'Dell et al., 1994).

It has been demonstrated that ruthenium complexes containing a ruthenium carbon double bond of the type shown in Fig. 3-5 are active catalysts for the metathesis of acyclic and cyclic olefins. The activity of the ruthenium complexes of the general structure shown below can be varied by changing the structure of the phosphine ligand (PR<sub>3</sub>), the substituent on the carbene carbon

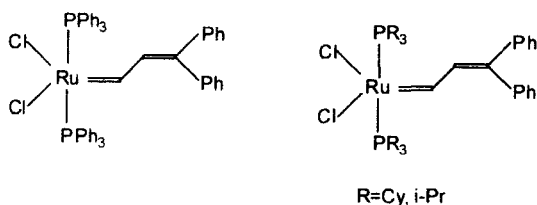
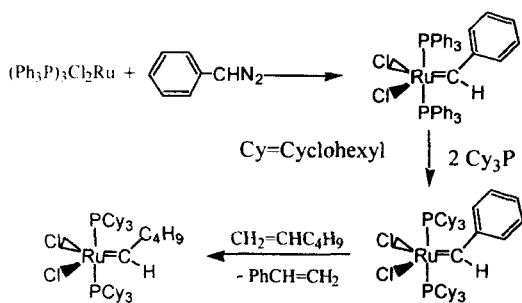


Figure 3-5.

( $R^1$ ), and the halide or anionic group (X). The catalysts with bulky alkyl phosphine and  $X = \text{Cl}$  are the most active (Nguyen et al., 1992; Wu et al., 1992; Nguyen and Grubbs, 1993) (Fig. 3-5).

The original catalyst (Grubbs et al., 1994) was prepared in approximately 70% yield from the reaction between diphenylcyclopropene and the tris(triphenylphosphine) ruthenium dihalide complex. The triphenylphosphine complex would polymerize norbornene and cyclobutenes without chain transfer and termination. As expected from earlier work with ill-defined systems, these systems were more tolerant of functional groups and protic impurities than the early metal analogs. Exchange of the triphenylphosphine ligand by tricyclohexylphosphine (or other bulky basic phosphines) proceeded cleanly and gave a much more active catalyst. This complex was active for the ROMP of unstrained olefins, and would catalyze acyclic olefin metathesis and ADMET polymerization.



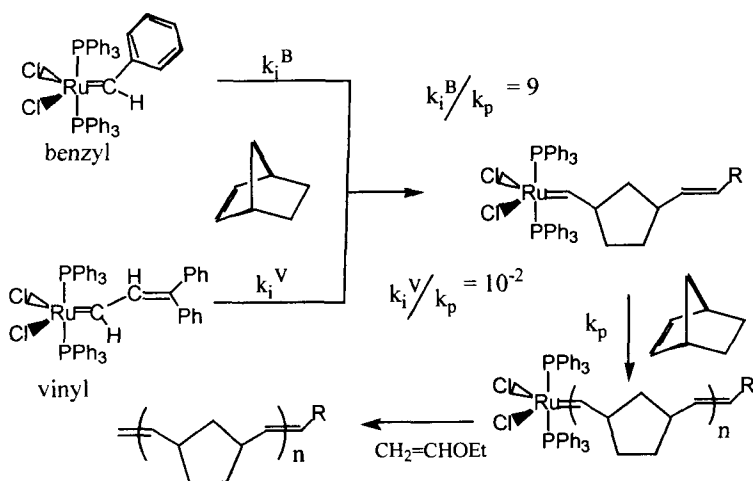
Scheme 3-2.

A new method, which uses phenyldiazomethane as the carbon source and tris(triphenylphosphine) rutheniumdichloride as the metal precursor, has resulted in an increase in the availability of an active catalyst (Schwab et al., 1996). The appropriate phosphine is incorporated by ligand exchange. These complexes are more reactive than the analogous vinylcarbene complexes, such as those shown in Fig. 3-5. The benzylidene complexes will react with terminal olefins to give the analogous metathesis carbene product, as shown in Scheme 3-2.

All these ruthenium carbene complexes polymerize norbornene in organic media, both in the absence and the presence of protic/aqueous solvents. The complexes are moderately stable in air, and they are stable in organic solvents in the presence of water, alcohol, acetic acid, or a diethyl ether solution of HCl. They do not undergo Wittig-type reaction with either ketone or aldehyde. These complexes catalyze the ROMP of *cis*-cyclooctene, cyclooctadiene, 7-oxonorbornene derivatives, and cyclopentene. In each of these cases, a propagating alkylidene can be observed via  $^1\text{H}$  NMR spectroscopy. The original vinylcarbene complexes produced polynorbornenes with polydispersities of  $\text{PDI} = 1.2 - 1.3$ . However, the benzylcarbene complexes gave polymers with  $\text{PDI} = 1.04$  (see Scheme 3-3). This difference can be traced to the increased reactivity of the benzylidene complex relative to the vinylidene complex so that the  $k_i^Y/k_p^Y$  for the vinylcarbene complex is less than  $10^{-2}$ , while the  $k_i^B/k_p^B$  for the benzylidene complex is 9.

The living propagating carbene can be observed throughout the reaction and the system passes all the required tests for a living polymerization.

The tolerance of these initiators to impurities and organic functionality has led to their wide use in the synthesis of well-defined polymers by ROMP and ADMET, and



$\text{PDI} = 1.3$  for vinyl and  $1.04$  from benzyl

Scheme 3-3.

for the synthesis of small molecules by cross metathesis of acyclic olefins and by ring-closing metathesis (RCM). This tolerance and the growing ease of synthesis has led to a number of potential commercial applications, since this family of ruthenium catalysts can now easily be prepared in multi-kilogram quantities.

### 3.3 ROMP Using Well-Defined Tungsten- and Molybdenum-Based Alkylidene Initiators

The design and synthesis of functional polymers, polymers whose properties depend to a significant extent on the functional group substituents along the backbone of the macromolecule, is an active area of research. The synthesis of these polymers through the polymerization of functionalized monomers is ideal, as it enables the direct incorporation of functionality into the polymer backbone and thus avoids the potential difficulty of chemical transformation on a polymeric substrate. In the case of ROMP (Grubbs and Tumas, 1989; Schrock, 1990a; Ivin, 1983), initial efforts in the

search for a catalyst system effective for the polymerization of functionalized substrates were met with limited success (Ivin, 1983). One overwhelming problem with most of the early transition metal ROMP catalysts was the high reactivity of the catalyst with any polar functionality present in the monomer. As a result, poisoning of the catalyst and polymerization became competitive processes. At present, polymers of commercial interest prepared via ROMP contain only an olefinic functionality, as illustrated in Fig. 3-6.

The preparation of such heteroatom-containing materials using classical metathesis catalysts proved difficult in the past, due to the sensitivity of these electrophilic metal complexes towards the heteroatom functionality. However, living ROMP catalysts have recently been prepared that are "deactivated" to an extent that they do not react with the functionality, but still react with the strained carbon-carbon double bond of the monomer. The tolerance of well-defined initiators towards functional groups also allows the use of functionalized styrenes as chain transfer agents (Schrock et al., 1989; Crowe et al., 1990; Mitchell, 1991; Hill-



myer and Grubbs, 1993) and functionalized benzaldehyde in the capping reaction (Bazan, 1990; Mitchell et al., 1991; Bazan and Schrock, 1991; Dounis, 1994). The key to controlled polymerization of norbornenes and norbornadienes is that, while  $M(\text{CH-}t\text{-Bu})(\text{NAr})(\text{O-}t\text{-Bu})_2$  initiators do not react rapidly with ordinary internal olefins, they do react rapidly with the strained double bond in norbornenes and norbornadienes (Fig. 3-7).

The living nature of these polymerizations can be conveniently monitored by  $^1\text{H}$  NMR spectroscopy. The downfield singlet arising from the alkylidene proton of the initiator gradually disappears and is replaced by a series of resonances corresponding to the propagating alkylidene protons, the number and multiplicities of which depend upon the nature of the monomer, including

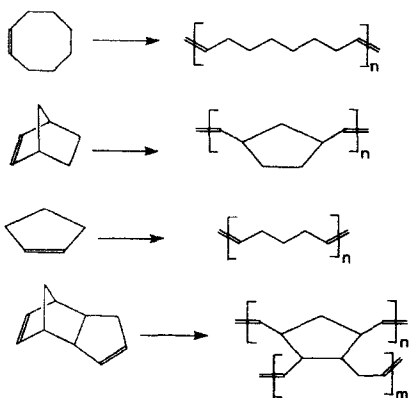


Figure 3-6.

the nature and disposition of any substituent, the arrangements of ligands around the active site, and the living polymer chain structure. These living polymers will react readily with aldehydes (e.g., benzaldehyde) to give the metal oxide in a Wittig-like capping reaction, as shown in Fig. 3-7. The polymers thus obtained have been shown to be essentially monodisperse (polydispersity indices as low as 1.03 for  $x=500$ ), i.e., the distribution about the average chain length ( $x$ ) is as narrow as possible, indicative of a well-behaved and irreversible living polymerization (Schrock, 1990 a).

In contrast, a completely reversible ROMP using the well-defined initiator  $(t\text{-BuO})_2\text{W}(\text{CH-}t\text{-Bu})(\text{NAr})$  (IV), has been reported for cyclopentene (Schrock et al., 1988b). In this case, the polymerization mixture at  $60^\circ\text{C}$  was reported to contain ~95% monomer, while at  $-60^\circ\text{C}$  the mixture contained ~95% polymer. When cyclopentene was removed under vacuum, the initiator was recovered in high yield. All these characteristics are typical of classical cyclopentene polymerization systems (Ivin, 1983).

For the polymerization of norbornene, the configuration about the first double bond in the polymer is solely *trans*, the polymer chain contains both *cis* (40%) and *trans* (60%) double bonds, and the Wittig reaction yields a double bond that is ~75% *trans* (Schrock, 1990 a).

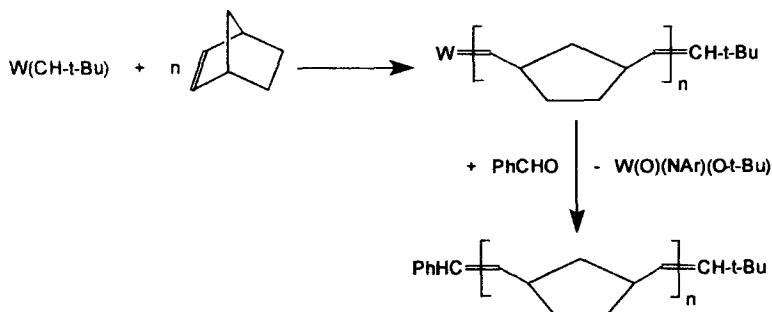


Figure 3-7.

Additional stereochemical complications in polynorbornene arise from the fact that two tertiary carbon atoms in norbornene [C(1) and C(4)] are chiral. Consequently, although the two C-C bonds at positions 1 and 4 are constrained to have a *syn* relationship, norbornenes can be opened to give polymers in which the configurations of those two carbon atoms occur in one of the two regular sequences where  $[(R,S)=(R,S)=(R,S)=]$  is *isotactic* and the alternative  $[(R,S)=(S,R)=(R,S)=]$  is *syndiotactic*, or be statistically distributed to give an *atactic* polymer (Fig. 3-8) (Ivin, 1983). Therefore, any given olefinic carbon atom can be in a double bond that is either *trans* and *racemic* or *meso*, or *cis* and *racemic* or *meso*. In practice, completely tactic polynorbornenes are, as yet, rare (Ivin, 1983; Draughton et al., 1985). Further substitution on the norbornene ring at a position unsymmetric with respect to the double bond creates the possibility of head-to-head (H, H), tail-to-tail (T, T), or head-to-tail (H, T) placement of repeat units in the polymer and leads to another level of stereochemical complexity (Ivin, 1983; Draughton et al., 1985).

Tungsten-based initiators do not appear to polymerize monomers that contain a variety of functionalities, but molybdenum-based systems will (Bazan et al., 1990, 1991a; Bazan and Albagli). The choice of solvent is an important factor in the ROMP of functionalized molecules. For

example, it is not possible to polymerize 5-cyanonorbornene with  $W(CH-t-Bu)(NAr)(O-t-Bu)_2$  or with  $Mo(CH-t-Bu)(NAr)(O-t-Bu)_2$  in a typical noncoordinating solvent such as toluene. In THF, however,  $Mo(CH-t-Bu)(NAr)(O-t-Bu)_2$  will polymerize 200 equiv. of 5-cyanonorbornene rapidly to give a homopolymer with a polydispersity of 1.05. THF may compete with the functionality for the metal and thereby inhibit a reaction between it and the alkylidene ligand. Another possibility is a bulk solvent effect which keeps the polar group pointed away from the metal and into the solution. A third possibility is that THF is intimately involved in opening the intermediate metallacycles formed in these reactions.

The rate of formation of a metallacycle is found to be greatly affected by substituents at the 7-position in norbornadiene (Schrock, 1990a). An interesting example is shown in Fig. 3-9. The reaction between  $Mo(CH-t-Bu)(NAr)(O-t-Bu)_2$  and 7-isopropylidene-2,3-dicarbomethoxynorbornadiene is slow at room temperature, approximately 350 times slower than the rate of polymerization of 2,3-dicarbomethoxynorbornadiene (Bazan et al., 1990). Only one equiv. reacts readily, even at 40 °C, i.e., the rate of the "first insertion" step, although slow, is very much greater than the rate of the "second insertion" step ( $k_p \approx 0$ ). The structure of this "first insertion" product was found to be *syn*, in

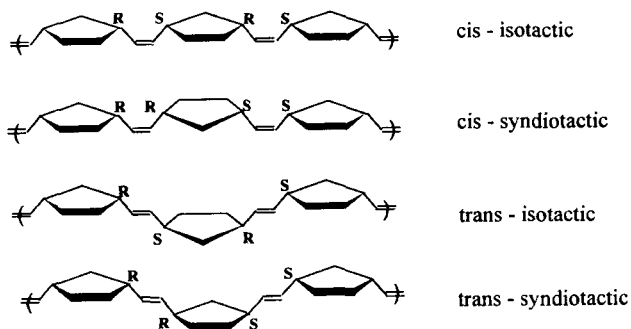


Figure 3-8.

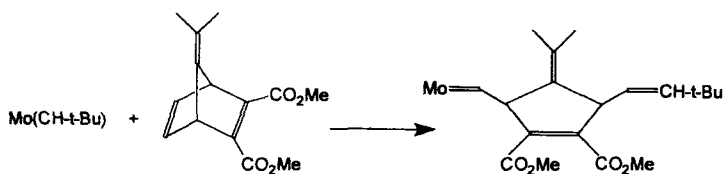


Figure 3-9.

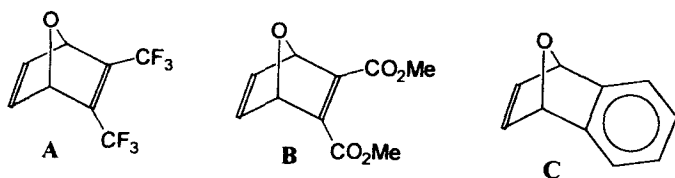


Figure 3-10.

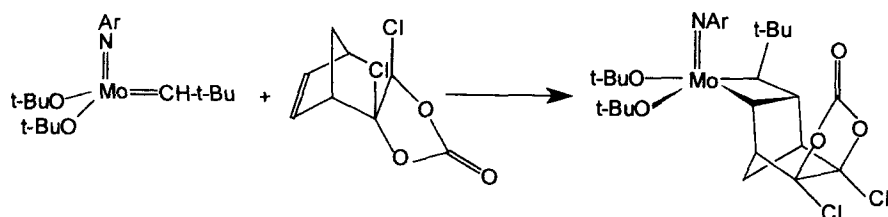


Figure 3-11.

which the isopropylidene group protects one side of the Mo-C bond while a carbomethoxy group protects the other side. Therefore this alkylidene is much less reactive towards a second equivalent of the monomer than the initial neopentylidene complex is.

It appears that norbornenes that have substituents at carbons 5 or 6, or 2,3-disubstituted norbornadienes, are those that yield relatively stable metallacycles, and the initial (*t*-butyl-substituted) metallacycle is more stable than subsequent metallacycles. 7-Oxanorbornadienes **A**, **B**, and **C**, shown in Fig. 3-10, react with  $\text{Mo}(\text{CH-}t\text{-Bu})(\text{NAr})(\text{O-}t\text{-Bu})_2$  to give isolable metallacyclobutane complexes. The metallacycle prepared from **A** is remarkably stable towards rearrangement to an alkylidene complex, that prepared from **B** is less so, and that prepared from **C** is the least stable (Schrock, 1990 a).

The first observable circumstance where metallacycle formation is reversible for a norbornene has been reported for the ROMP of 5,6-dichloro-5,6-carbonatonorbornene. The monomer reacts with  $\text{Mo}(\text{CH-}t\text{-Bu})(\text{NAr})(\text{O-}t\text{-Bu})_2$  to give an observable metallacycle, as illustrated in Fig. 3-11 (Schrock, 1990 a). When this metallacycle is heated, the monomer is regenerated to give ~50% of the starting neopentylidene complex.

Benzonorbornadiene reacts rapidly with  $\text{Mo}(\text{CH-}t\text{-Bu})(\text{NAr})(\text{O-}t\text{-Bu})_2$  (Fig. 3-12) to yield the living polymer (Bazan et al., 1990). The alkylidene resonance at 11.23 ppm is replaced by a relatively complex set of alkylidene resonances further downfield. A plausible explanation is that when a flat ring is present,  $H_\alpha$  is sensitive to the *cis* or *trans* configuration of at least the next double bond in the chain, and two different alkylidene rotamers are present.

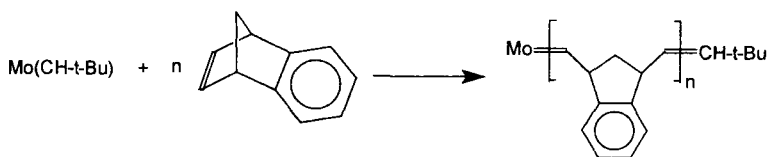


Figure 3-12.

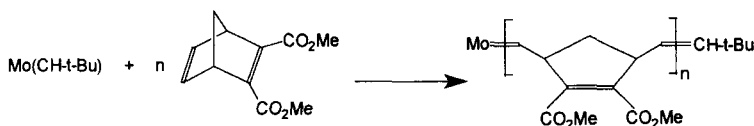


Figure 3-13.

The percentage of *trans* double bonds is 76%. GPC analysis of the polymers prepared showed polydispersities of  $\sim 1.05$ . Polybenzonorbornadiene with a degree of polymerization of up to 500 is soluble in toluene or dichloromethane and, except for its expected sensitivity to oxygen (El-Saafin and Feast, 1982), the polymerization proceeds in a well-behaved manner. These properties contrast with those reported by Cannizzo and Grubbs (1988) for polybenzonorbornadiene prepared with a titanium catalyst. Insolubility became a limiting factor, apparently due to differences in the stereochemistry when fewer than 10 equivalents of benzonorbornadiene had been polymerized. Benzonorbornadiene has also been polymerized by classical catalysts (e.g.,  $\text{WCl}_6/\text{SnMe}_4$ ) (El-Saafin and Feast, 1982). In this case, however, broad molecular weight distributions and low solubilities were observed and ascribed (in part) to oxidation of the polymer in air. Therefore it appears that polymerization of benzonorbornadiene by  $\text{Mo}(\text{CH-}t\text{-Bu})(\text{NAr})(\text{O-}t\text{-Bu})_2$  is the most successful of several routes investigated for the synthesis of polybenzonorbornadiene. In general, complications due to oxidation may arise, in part from the fact that the tertiary proton in the polymer is both allylic and benzylic.

It has been reported that, although 5,6-dicarbomethoxynorbornadiene (DCNBD)

could not be polymerized in a controlled manner by tungsten initiators, the addition of DCNBD to a molybdenum initiator quantitatively converted it into polymer with a low polydispersity index (Fig. 3-13), characteristic of a living polymerization catalyst system (Schrock, 1990a; Bazan et al., 1990). The ratio of the rate of propagation to the rate of initiation ( $k_p/k_i$ ) was found to be  $3 \pm 0.3$ . Carbon NMR spectra suggest that the double bonds are 90–95% *trans*. The polymer appears to be thermally unstable in air, since the glass transition ( $\sim 140^\circ\text{C}$ ) does not appear to be reproducible. Instability was confirmed by TGA. The polymer begins to decompose at  $200^\circ\text{C}$  and degrades rapidly at  $300^\circ\text{C}$ .

Cyanonorbornenes, such as **V–VIII** shown in Fig. 3-14, have also been investigated and in some cases will undergo polymerization (Feast et al., 1995). For example, monomer **VI** gives a soluble polymer containing 97% *trans* vinylenes from which it is possible to cast tough transparent films for which DSC shows no  $T_g$  below the decomposition temperature of  $250^\circ\text{C}$ . This work represents the first successful polymerization of polycyanomonomers using well-defined initiators.

The types of substituents in norbornene monomers appear to have considerable impact on the outcome of the initiation and propagation steps in ROMP; for norbornene

and monosubstituted norbornenes, the rate of propagation is found to be faster than the rate of initiation. However, it has been reported that the rate of propagation could be modified by the addition of compounds such as trimethylphosphine (Wu et al., 1992) and quinuclidine (Schlund et al., 1989). They bind to a significantly greater extent to the propagating alkylidene complex than to the initial alkylidene complex, and thereby slow down the rate of propagation significantly more than the rate of initiation.

Fluorinated cyclic olefins undergo ROMP using classical initiator systems based upon a transition metal chloride and a Lewis acid cocatalyst. However, the classical initiators have suffered from disadvan-

tages that include lack of molecular weight control and an element of irreproducibility. Recent advances in the synthesis of well-defined living ROMP initiators have made it possible to polymerize fluorinated monomers in a well-controlled manner (Schrock, 1990a; Bazan et al., 1990). Thus ROMP of a wide range of fluorinated bicyclic olefins using a well-defined Schrock's initiator based on  $\text{Mo}(\text{CH}-t\text{-Bu})(\text{NAr})(\text{O}-t\text{-Bu})_2$ , as shown in Fig. 3-15, has been reported.

### 3.4 ROMP Using Ruthenium-Based Initiators

#### 3.4.1 Aqueous ROMP

The sensitivity of organometallic compounds to oxygen, water, and heteroatom functionalized substrates has often hampered their evolution from research laboratories to full scale industrial processes. Highly Lewis acidic transition metal compounds, such as  $\text{WCl}_6$  and most of the well-defined initiators introduced by Osborn or Schrock, although more selective towards olefin metathesis, are still subject to deactivating side reactions. These limitations are

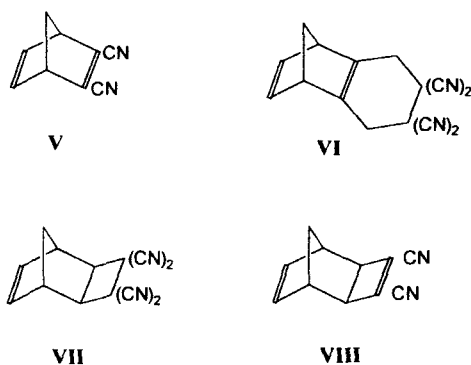


Figure 3-14.

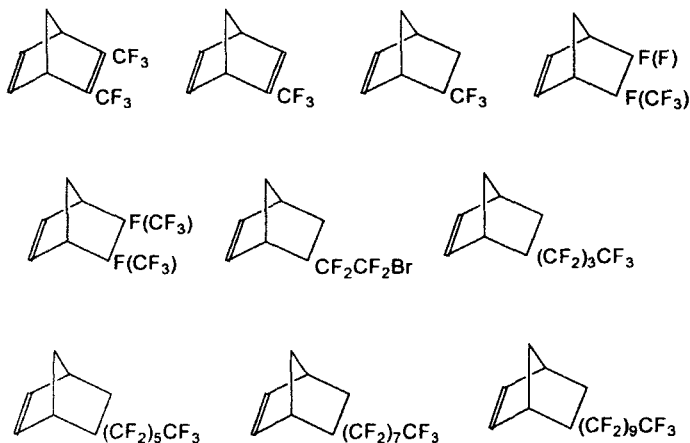


Figure 3-15.

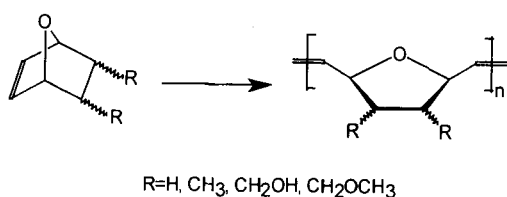


Figure 3-16.

primarily the result of reactions between the heteroatoms in the monomers and the typically oxophilic metal centers of the ROMP initiators (these side reactions include Wittig-type reactions with carbonyl groups and cationic ring opening of the heterocycle) (Brown-Wensley et al., 1983; Wittbecker et al., 1960).

As a result of the earlier work of Michelotti, and Rinehart (Michelotti and Keaveneey, 1965; Michelotti and Carter, 1965; Rinehart and Smith, 1965) on ill defined-catalysts, Grubbs and co-worker studied the ROMP of 7-oxanorbornene derivatives (Fig. 3-16) in organic solvents by using a variety of transition metal salts (Novak and Grubbs, 1988 a, b). The most successful catalysts were systems based on the group VIII metal complexes, such as  $\text{RuCl}_3(\text{hydrate})$  and  $\text{OsCl}_2(\text{hydrate})$ .

Polymerizations using these group VIII metals are sometimes preceded by a lengthy initiation period. It is during this initiation period that a small amount of reactive metal carbene is formed, which then very rapidly polymerizes the cyclic olefin present. During the efforts to decrease this initiation period (typically 22–24 h for **IX** in organic solvents), it was found that rigorous exclusion of water from the reaction mixture actually had an unexpected effect. Rather than deactivating these metal catalysts, water actually acted as a cocatalyst by dramatically decreasing the initiation period required for the reaction. This unusual finding eventually led to the discovery that the polymerization of 7-oxanorbornene deriva-

tives proceeds rapidly in water alone to produce the desired ROMP polymer in nearly quantitative yields. Initiation times decreased from 22–24 h, when using organic solvents, to 30–35 min in aqueous solution (Novak and Grubbs, 1988 a, b). Further, on examining the used aqueous ruthenium solutions after an initial polymerization, it was reported that not only is the solution recyclable, but these used catalysts actually become more active in the initiation of subsequent polymerizations. The initiation period drops from the initial value of 37.5 min to a limiting value (after two to three polymerizations) of only 10–12 s. Solutions containing these aqueous catalysts have been recycled for up to 14 successive polymerizations without any detectable loss of activity (Novak and Grubbs, 1988 a, b).

The aqueous polymerization of 7-oxanorbornene derivatives (**IX**) by the very active  $\text{Ru}(\text{H}_2\text{O})_6(\text{tos})_2$  (where  $\text{tos} = p\text{-toluenesulfonate}$ ) salt shows the same basic trends. When  $n$  equivalents of **IX** are allowed to react with  $\text{Ru}(\text{H}_2\text{O})_6(\text{tos})_2$  in  $\text{D}_2\text{O}$ , ( $n-1$ ) equiv. of **IX** are polymerized, and conversion of the catalyst to the mono-olefin adduct  $\text{Ru}(\text{H}_2\text{O})_5(\text{II})(\text{tos})_2$  (**X**) is observed by NMR (Fig. 3-17). Aqueous solutions of **X** are highly active in subsequent polymerizations, displaying the same rapid initiation times (10–12 s) as the limiting initiation times observed for the recycled  $\text{Ru}^{3+}$  solutions. The resulting poly(7-oxanorbornene) is of keen interest due to its potential ionophoric properties (Schultz et al., 1988; Kyba et al., 1977; Lundberg et al., 1966; Blonsky et al., 1988). The simple ruthenium coordination complex  $\text{Ru}^{\text{II}}(\text{H}_2\text{O})_6(\text{tos})_2$  ( $\text{tos} = p\text{-toluenesulfonate}$ ) was found to be the most active catalyst employed (Hillmyer et al., 1992), giving high molecular weight, low polydispersity materials in almost quantitative yields. In addition, the catalyst is active for the polymerization of a variety

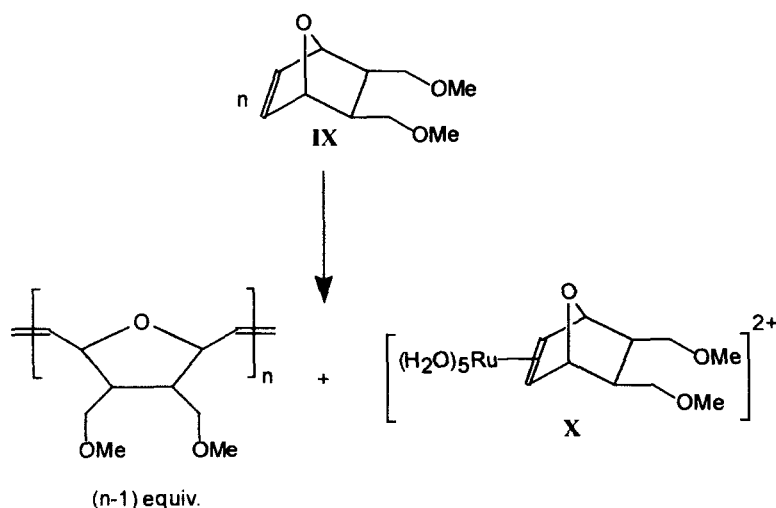


Figure 3-17.

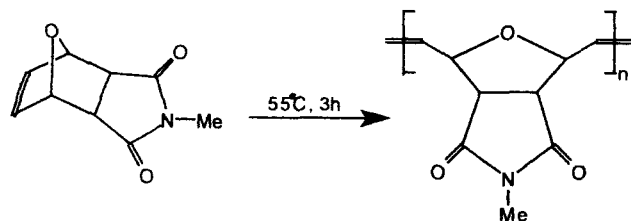


Figure 3-18.

of 7-oxanorbornene derivatives, including hydroxyl-, carboxyl-, and alkoxy-substituted monomers (Novak and Grubbs, 1988 b). The scope of the aqueous ruthenium polymerization system was expanded to include the polymerization of carboximide-functionalized 7-norbornenes (Hillmyer et al., 1992). The polymerization was accomplished under mild conditions using the ruthenium(II) catalyst  $\text{Ru}^{\text{II}}(\text{H}_2\text{O})_6(\text{tos})_2$  to yield high molecular weight polymer in near quantitative yields (Fig. 3-18). The resultant polymer possessed a high degree of thermal and oxidative stability, as well as a relatively high glass transition temperature (225 °C).

Attempts to polymerize the relatively deactivated anhydride in dry organic solvents resulted in catalyst deactivation. It was found, however, that the monomer could be polymerized in aqueous solution (Novak et al., 1992), as shown in Fig. 3-19.

The polymerization process is quite surprising, given that hydrolysis of the anhydride moiety occurs simultaneously producing norbornene diacid, a known poison for other catalyst systems, as well as the desired polyacid materials.

The microstructures of polymers prepared from the ROMP of 7-oxanorbornene, endo-5-(methoxymethyl)-7-oxanorbornene, and *exo,exo*-5,6-bis(methoxymethyl)-7-oxanorbornene were studied by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy (Benedicto et al., 1992). Polymers prepared from  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  have a high *trans* double bond content and are believed to be highly *isotactic*. Polymers prepared from  $[\text{Ru}(\text{H}_2\text{O})_6](\text{tosylate})_2$  exhibit roughly equal amounts of *cis* and *trans* double bonds which are randomly distributed in the polymer chain and *atactic*.

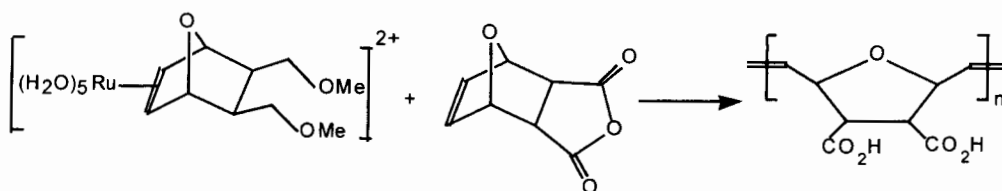


Figure 3-19.

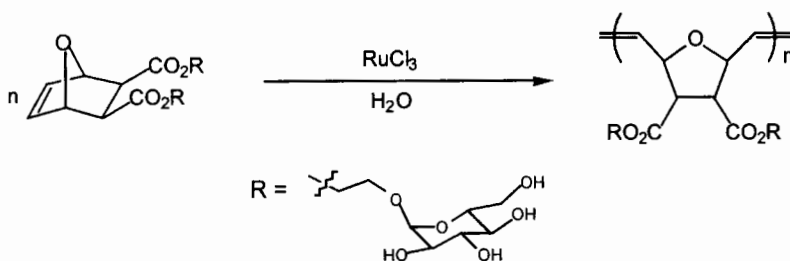


Figure 3-20.

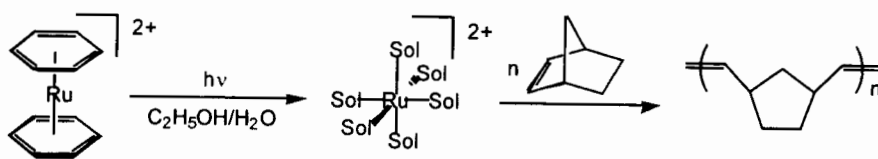


Figure 3-21.

Feast and co-worker have also reported the aqueous ROMP of *exo,exo*-5,6-bis(methoxymethyl)-7-oxanorbornene using the trichlorides of ruthenium, iridium, and osmium as catalysts (Feast and Harrison, 1991). The inclusion of *cis*-but-2-ene-1,4-diol or its dimethyl ether in the reaction mixture had a marked effect on both tin induction times and the reactivity, and allowed control of the molecular weight of the product polymers. The yields of polymer obtained using ruthenium(III) and osmium(III) chloride were reported to be good (95%), whereas those from experiments using iridium(III) chloride were poor (2%). The carbon NMR spectra provided unambiguous evidence that all samples produced in this work contain predominantly *trans* vinylenes, 60% for  $RuCl_3 \cdot 3H_2O$ , 75% for  $OsCl_3 \cdot 3H_2O$ , and 90% for  $IrCl_3 \cdot 3H_2O$ .

A mechanism has been proposed (Novak and Grubbs, 1988 b), which involves the dis-

proportionation of some of the  $Ru^{3+}$ -olefin complex to provide an  $Ru^{2+}$ -olefin complex and an  $Ru^{4+}$  species which is trapped by additional  $Ru^{3+}$ . The olefin- $Ru^{2+}$  complex thus produced initiates the observed polymerization chemistry. A ruthenium alkylidene complex is postulated as the propagating species during these polymerizations (France et al. 1993 a, b). However, little is known about the structure and reactivity patterns of this active species or about the initiation mechanism leading to its formation.

In a recent application of these catalysts, Kiessling (Schuster et al., 1997; Manning et al., 1997) has reported the preparation of a bioactive polymer (Fig. 3-20).

Karlen et al. (1995) have described a photoinitiated ROMP (PROMP) system in water/ethanol mixtures using a variety of ruthenium complexes with photo-labile ligands. For example, the irradiation of



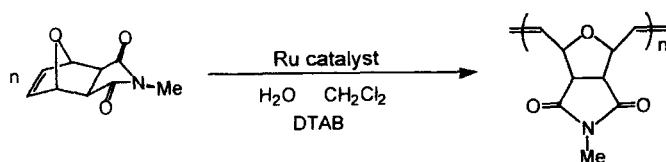


Figure 3-22.

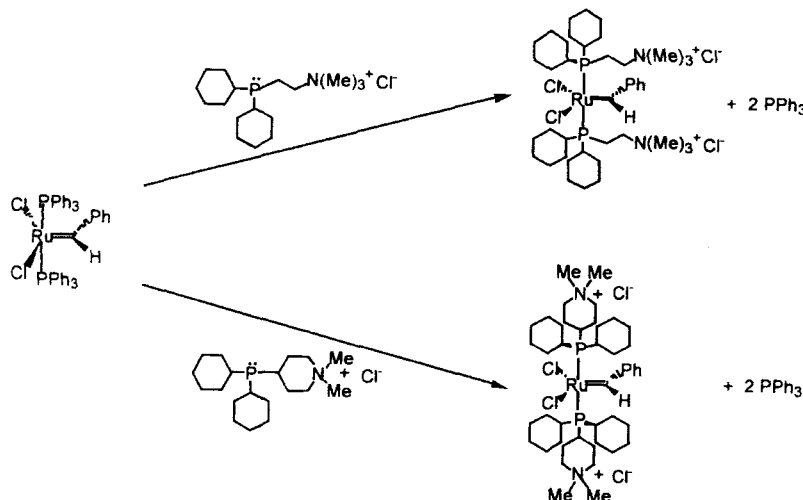


Figure 3-23.

$[\text{Ru}(\text{CH}_3\text{CN})_6](\text{tos})_2$  or  $[(\text{C}_6\text{H}_5)_2\text{Ru}](\text{tos})_2$  leads to partially and fully solvated  $\text{Ru}^{2+}$  species, which initiate the ROMP of highly strained olefins, presumably in the manner outlined above (Fig. 3-21).

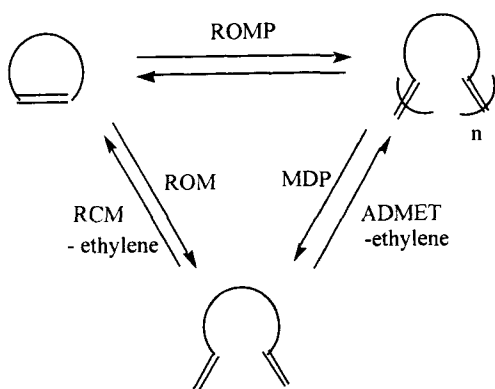
The lessons learned from the studies of these ill-defined catalysts led to the synthesis of the well-characterized catalysts discussed in the Sec. 3.3. With these well-defined complexes, which prove to be “living” in organic solvents, came the opportunity to examine the potential for “living polymerization” in water using well-defined complexes. Since the initially prepared complexes were insoluble in water, a suspension polymerization was carried out using an emulsifier and a small amount of organic solvent in water (Fig. 3-22). These systems led to high molecular weight polymer of narrow polydispersity ( $\text{PDI} = 1.10$ ) (Lynn et al., 1996).

Under these conditions, a plot of molecular weight against monomer/complex was

linear, and it was demonstrated that the systems would reinitiate with little loss of growing polymer chains. These observations demonstrated the tolerance of these systems to water and opened the possibility of controlled polymerization using a variety of monomers. The results also encouraged the synthesis of water-soluble initiators.

To accomplish this goal, a family of water-soluble phosphines, which contain bulky trialkyl groups of the type required to produce highly active metathesis catalysts, was prepared (Fig. 3-23). These complexes allow for emulsion polymerizations to be carried out. With these initiators, the propagating species can be observed, the chains can be reinitiated, and the polymer is of low polydispersity (Mohr et al., 1996; Lynn et al., 1997).

Consequently, the study of an ill-defined system led to the development of a well-defined initiator, which resulted in a living, well-controlled polymerization system.



Scheme 3-4.

### 3.4.2 Other Metathesis Reactions

A related set of reactions that involve acyclic olefins can be used to prepare interesting polymer structures as well as small molecules. It is informative to define the relationship of these reactions to ROMP (Scheme 3-4). One of these, ADMET polymerization, is developing into a very useful process. This topic will not be covered further, since another chapter in this book is devoted to this topic (Wagener et al., 1991).

#### 3.4.2.1 Telechelic Polymers

A process for preparing polymers which exploit the mechanism of metathesis is the formation of telechelic polymers by the

cross-metathesis of cyclic and functionalized acyclic olefins (Fig. 3-24) (Hillmyer and Grubbs, 1993; Hillmyer et al., 1997).

The molar mass of the resulting polymer is easily controlled by changing the ratio of the cyclic to acyclic olefin, and the resulting polymers contain two functional end groups, as is required for the synthesis of high molecular weight condensation polymers. Since the ruthenium catalysts tolerate a variety of functional groups, this process can be used to prepare a variety of telechelics with a selection of useful terminal functional groups.

#### 3.4.2.2 Ring-Closing Olefin Metathesis (RCM)

The transition metal alkylidene-catalyzed olefin metathesis reaction has been the focus of intense interest in recent years from the standpoint of both mechanism and polymer synthesis. In contrast, use of this transformation in organic synthesis has been limited until recently (Grubbs and Pine, 1991; Stille and Grubbs, 1986; Stille et al., 1990). As part of a broader program directed towards establishing transition metal alkylidenes as versatile reagents for organic chemistry, Fu and Grubbs (1992 a) reported the successful application of catalytic olefin metathesis to the generation of a variety

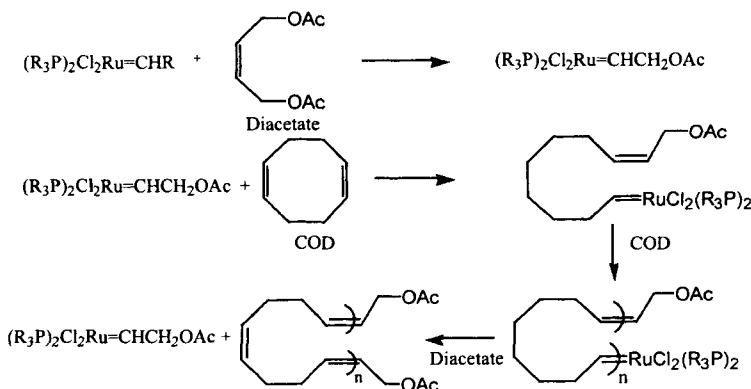


Figure 3-24.

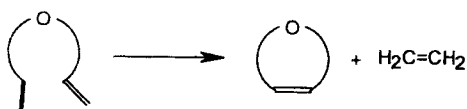
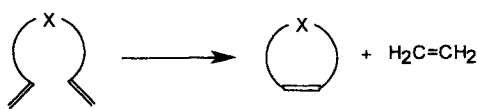


Figure 3-25.

of unsaturated heterocycles. Their approach to the synthesis of unsaturated oxygen heterocycles involves ring-closing metathesis of diene-ethers to generate a cyclic and an acyclic olefin (Fig. 3-25). In contrast to the normal situation, where new methods are developed in synthetic organic chemistry and then applied to polymer chemistry, in this case the catalysts developed for polymerization are now becoming widely used in the synthesis of natural products (Grubbs et al., 1995).

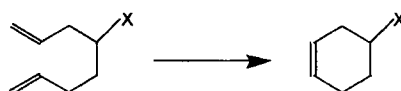
The treatment of a diallyl ether with catalyst  $\text{Mo}(\text{CH-}i\text{-Bu})(\text{NAr})[\text{OCMe}(\text{CF}_3)_2]_2$  at 20 °C afforded the 2,3-dihydrofuran. Catalytic ring-closing metathesis also afforded efficient access to dihydro pyrans. Thus catalytic ring-closing metathesis of diene-ethers provides access to an array of unsaturated oxygen heterocycles (Fu and Grubbs, 1992 a). Grubbs and co-workers demonstrated that the ruthenium carbene is also an efficient catalyst for ring-closing olefin metathesis (Fu et al., 1993). This new catalyst possesses two important advantages over the molybdenum-based initiator: diminished sensitivity to atmospheric oxygen and moisture, and (Stille and Grubbs, 1986) increased tolerance of most functionalities. This has led to the application of ring-closing metathesis to the generation of a variety of other cyclic structures (Fu et al., 1993; Fu and Grubbs, 1992 b), as shown in Fig. 3-26.

Treatment of dienes with 0.1–4 mol% of ruthenium initiator at room temperature resulted in the formation of a variety of unsaturated heterocycles and carbocycles in good yields. The catalyst efficiently generates five-, six-, and seven-membered nitrogen heterocycles, and it tolerates common pro-



$\text{X}=\text{O}, \text{N}, \text{C}$

Figure 3-26.



$\text{X}=\text{CO}_2\text{H}, \text{CH}_2\text{OH}, \text{CHO}$

Figure 3-27.

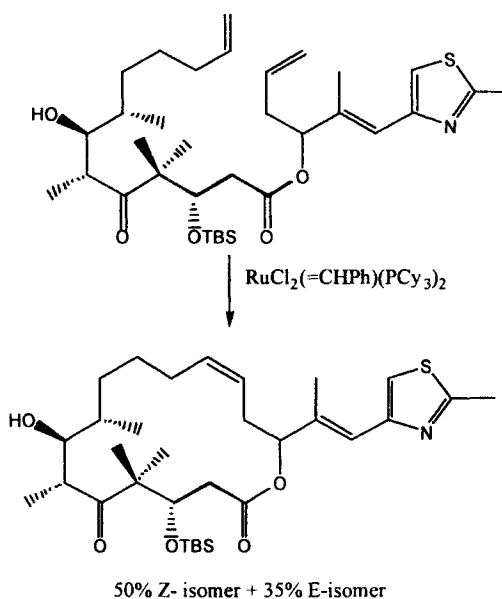


Figure 3-28.

tecting groups, including trifluoroacetyl, *tert*-butoxycarbonyl, and benzyl.

Ruthenium carbene is remarkably tolerant of functional groups. In contrast to the previously studied molybdenum catalyst, which is known to react with acids, alcohols, and aldehydes, the ruthenium catalyst is stable to these functionalities. Thus treatment of the illustrated dienes with the ruthenium catalyst leads to clean cyclization to the substituted cyclohexenes (Fig. 3-27) (Fu et al., 1993).

Over the past couple of years, this reaction has become a major tool for the synthesis of complex biomolecules and, during the past 1.5 years, over 40 papers have appeared which outline a number of the uses of this reaction. Of particular importance is the application of these reactions in the construction of medium to large rings. An impressive example is shown in Fig. 3-28 (Yang et al., 1997).

### 3.5 Materials via ROMP

#### 3.5.1 Conducting Polymers

It has long been known that conjugated organic polymers can have semiconducting properties (Berets and Smith, 1968). The work of Shirakawa and of MacDiarmid and co-workers (Shirakawa and Keda, 1971; Shirakawa et al., 1977) has led to the realization that polymers such as polyacetylene can be produced as flexible semiconducting films, which can be made highly conducting by either oxidation or reduction. The material is air-sensitive, being fairly rapidly oxidized to a point where its interesting electrical properties are lost; once made, it is infusible and insoluble and therefore fabrication and morphological modification (e.g., orientation) present fairly formidable

problems. It is therefore desirable to prepare polymers that are soluble and amenable to conventional purification and fabrication techniques, but which can be converted easily and quantitatively to polyacetylene.

An effective and widely adopted solution to this problem is the Durham precursor route (Edwards et al., 1984; Feast and Winter, 1985) to polyacetylene, in which a tricyclic triene monomer is subjected to ROMP at the cyclobutene double bond using a  $WCl_6/Me_4Sn$  catalyst to give a high molecular weight soluble precursor polymer, which can be purified and analyzed using standard polymer characterization techniques. The precursor can then be converted in a controlled manner to polyacetylene in a variety of morphologies (Bott et al., 1985, 1986; Edwards et al., 1984; Feast and Winter, 1985) by a symmetry allowed elimination of hexafluoroxylylene (Fig. 3-29).

This method was an important breakthrough in polyacetylene research, since it could be employed to prepare oriented polyacetylene films by stretching the precursor polymer film before the retro-Diels-Alder reaction (Kahlert and Leising, 1985; Montaner et al., 1988; Perego et al., 1985); a significant advantage over classical "Ziegler-Natta" methods of preparing polyacetylene (Chien, 1984). However, the nature of classical metathesis catalysts in general is not

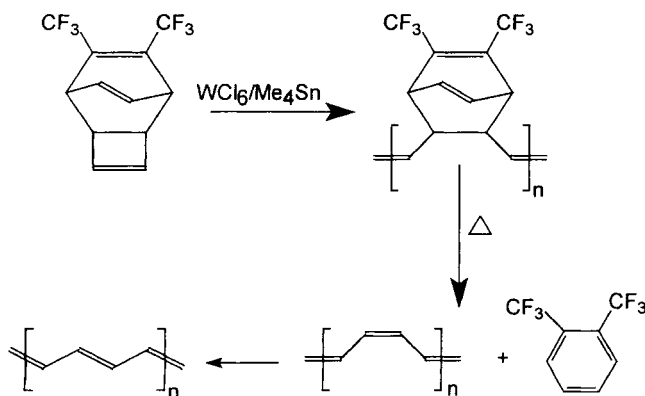


Figure 3-29.

well understood at a molecular level. Therefore their activity cannot be controlled to yield polymers with a relatively narrow distribution of predictable molecular weights, or block copolymers.

Using the well-defined molybdenum and tungsten initiators, Schrock was able to exploit this methodology to prepare polyenes with a variety of conjugated chain lengths (Knoll et al., 1988; Knoll and Schrock, 1989; Park et al. 1991), and was further able to show that they could be incorporated into low polydispersity di-blocks containing up to 100 equivalents of norbornene (Krouse and Schrock, 1988). More recent developments have witnessed microphase-separated block copolymers incorporating polyacetylene as the central block (Saunders et al., 1991), as well as polyacetylene attached to microelectrodes (Ofer et al., 1991). Grubbs and co-workers have shown that polyacetylene can be accessed via the ROMP of cyclooctatetraene (COT) (Klavetter and Grubbs, 1988) and substituted cyclooctatetraene (Ginsburg et al., 1989; Saylor et al., 1990; Gorman et al., 1993; Jozefiak et al., 1993), using Schrock's tungsten hexafluoro-*t*-butoxide initiator, in which the monomer is polymerized in the neat state to give a free-standing film (Fig. 3-30). The

polymerization can be conducted on substrates other than glass: metal, plastics, and cellulose have proved to be effective. Polyacetylene billets (cylinders, 1 mm diameter) have also been prepared, employing thin teflon tubing as the mold. Poly-COT films were oxidatively doped by exposure to iodine to conductivities greater than  $10^2 \text{ ohm}^{-1} \text{ cm}^{-1}$ .

An alternative precursor approach is the polymerization of benzvalene (Fig. 3-31) (Swager et al., 1988), the ring-opened product of which rearranges by heat, light or  $\text{HgCl}$  to polyacetylenic materials with conductivities ranging from  $10^{-8}$  to  $10^{-7} \text{ S cm}^{-1}$  before doping and 0.1 to  $1.0 \text{ S cm}^{-1}$  after doping with iodine.

An interesting variation is provided by the ROMP of 3,4-diisopropylidenecyclobutene (Swager and Grubbs, 1989), which affords a novel cross-conjugated polymer (Fig. 3-32) which is colorless.

Poly(3,4-diisopropylidenecyclobutene), as an air-sensitive clear film or white powder, was synthesized by ROMP of 3,4-diisopropylidenecyclobutene using titanocene methylidene sources as catalysts.

Poly(1,4-phenylvinylene) (PPV) is another polymer attractive for its high electrical conductivity when doped (ca.  $5000 \text{ S cm}^{-1}$ ). It also possesses a large third-order

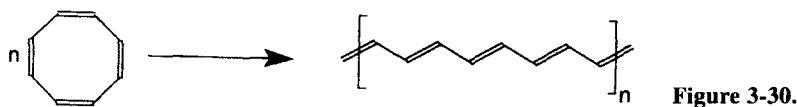


Figure 3-30.

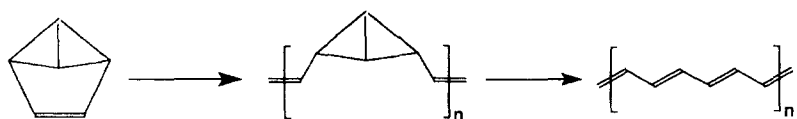


Figure 3-31.

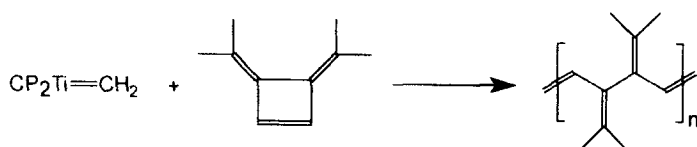


Figure 3-32.

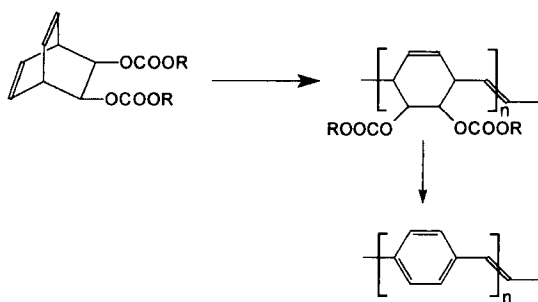


Figure 3-33.

non-linear optical response and photo- and electro-luminescence in the visible region. However, its extended planar topology renders it infusible and insoluble in nonreactive media and limits possibilities for post-synthesis fabrication of the material. Grubbs and co-workers have described a precursor synthesis (Fig. 3-33) which exploits the ‘living’ ROMP of bis(carboxylic ester) derivatives of bicyclo[2.2.2]octadienes using Schrock’s molybdenum hexafluoro-*t*-butoxide initiator (Conticello et al., 1992).

The precursor polymers possess approximately equal distributions of *cis* and *trans* linkages and narrow molecular weight distributions. Thermal treatment of an optically clear, coherent film of the precursor polymer results in free-standing PPV containing all-*trans* vinylene linkages.

### 3.5.2 Stereoregular Fluoropolymers

Polymerization of bis(trifluoromethyl) norbornadiene (BTFMND) (**XI**, Fig. 3-34), initiated by Schrock alkylidenes  $\text{Mo}(\text{CH}-t\text{-Bu})(\text{NAr})(\text{OR})_2$ , gives all *trans* poly(BTFMND) when  $\text{R} = t\text{-butyl}$  (Bazan et al., 1989, 1990) (i.e., **XIIa** initiation, see Fig. 3-34) and all *cis* poly(BTFMND) when  $\text{R} = \text{hexafluoro-}t\text{-butyl}$  (Feast et al., 1992 a) (i.e., **XIIb** initiation).

All *trans* polymer shows behavior that would be expected for a semicrystalline

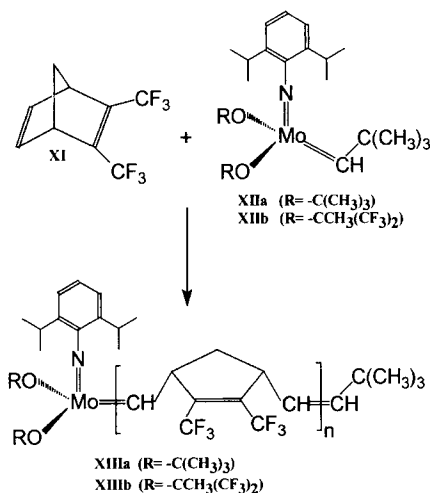


Figure 3-34.

thermoplastic. DSC studies reveal a well-defined  $T_g$  at  $97^\circ\text{C}$  and a broad melting endotherm at  $200^\circ\text{C}$ , the shape and area of which is dependent on the sample history. In samples precipitated from solution, the  $T_g$  transition is not particularly marked and the melting endotherm is consistent with the presence of multiple melting transitions. In melt-quenched samples the  $T_g$  transition is marked and the melting peak area is small. The melting peak area increases on prolonged annealing at  $180^\circ\text{C}$  (72 h), indicating a slow ordering process which is consistent with low chain mobility in the solid state. All earlier *atactic* samples were amorphous and only exhibit a well-defined  $T_g$  at  $125^\circ\text{C}$ . Dynamic mechanical thermal analysis of solution-cast films of both *tactic* and *atactic* samples show no energy dissipation peaks below  $T_g$ , indicating that in the solid state both are relatively stiff polymers with little or no motion below  $T_g$ . All-*cis* polymer exhibits a well-defined  $T_g$  at  $145^\circ\text{C}$  and no melting endotherm is observed.

Fibers for all-*trans* polymer can be drawn from the melt exhibiting 500% elongation on stretching, whereas fibers drawn from

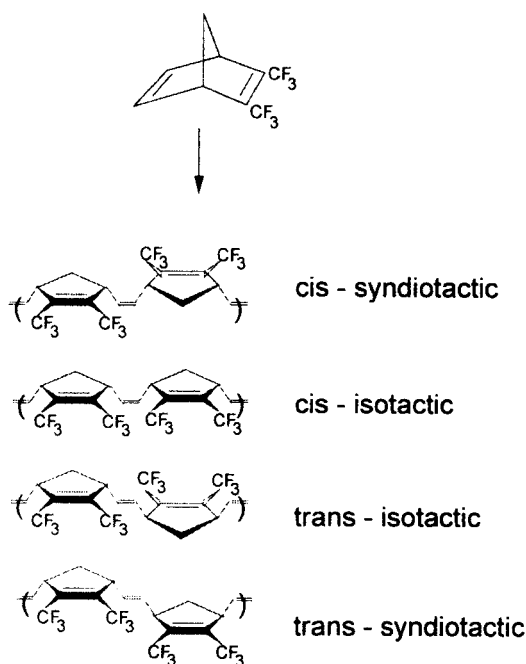


Figure 3-35.

*atactic* polymer prepared by  $\text{WCl}_6/\text{Me}_4\text{Sn}$  are weak and cannot be stretched.

Detailed  $^{13}\text{C}$  NMR analysis showed that the all-*trans* polymer is 92% *tactic* and the all *cis* polymer is 75% *tactic*. It has recently been shown that an initiator with a binaphthol replacing the two alkoxides and the arylimido isopropyl groups replaced by methyls gives poly(BTFMND) with 100% *cis*-vinylenes, which is also 100% *tactic* (McConville et al., 1993). Schrock and co-workers (O'Dell et al., 1994) have reported that all-*trans* norbornadiene polymers are *syndiotactic* and that all-*cis* norbornadiene polymers are *isotactic* regardless of the nature of the substituents in the monomers.  $^{13}\text{C}$  NMR analysis of all-*trans* poly(BTFMND) did not allow an assignment of its microstructure and, despite its high *tacticity*, its degree of crystallinity was too low to obtain X-ray diffraction data capable of reliable analysis. The all-*trans* polymer displayed a remarkably high relaxed dielectric constant

$\epsilon_R$  (greater than 40, cf. PVDF ca. 15), the all-*cis* polymer displaced a relatively low relaxed dielectric constant ( $\epsilon_R$  ca. 6), whereas the *atactic* polymer made via  $\text{WCl}_6/\text{Me}_4\text{Sn}$  initiation (54% *trans*-vinylene content) showed an  $\epsilon_R$  value of ca. 16 (Davies et al., 1995). The explanation of this large difference requires that in the *trans* polymer the polar bis(trifluoromethyl)cyclopentenyl rings in the chain (Fig. 3-35) can act in a collaborative reinforcing sense in response to an electric field, whereas in the *cis* polymer their individual effects tend to cancel each other out (Davies et al., 1992). This allowed an assignment of *syndiotacticity* unambiguously to all-*trans* and, with a degree of uncertainty, to all-*cis* polymers. The assignment of the tacticity of the all-*cis* polymer has proved to be more problematic since, although there is only one way to obtain a very high  $\epsilon_R$  value (cooperative reinforcement of individual ring effects), there may be several ways of effecting cancellation of dipoles and consequently low  $\epsilon_R$  value (Davies et al., 1995).

The potentially high polarity of fluorinated polymers led to the investigation of the pyroelectric properties of these materials for possible application as active components in various types of electrical devices, particularly heat sensors, electromagnetic radiation detectors, and thermal imaging systems. Much of the work on piezoelectric and pyroelectric behavior of polymers has been focused on poly(vinylidene fluoride) (PVDF). *Trans-syndiotactic* poly(BTFMND) has a high permittivity, greater than 40 above  $T_g$ , and a saturation polarization approaching  $20 \text{ mC m}^{-2}$  with a pyroelectric coefficient approaching  $6 \mu\text{C m}^{-2} \text{ K}^{-1}$ . While these values are less than for PVDF ( $50 \text{ mC m}^{-2}$  and  $30 \mu\text{C m}^{-2} \text{ K}^{-1}$ , respectively), the low  $\tan \delta$  ( $<0.001$ ) and permittivity at ambient temperature ( $\epsilon_U = 2.6$ ) allows favorable comparison with PVDF.

One figure of merit,  $F_D$ , [ $F_D = \gamma(\epsilon \tan \delta)^{1/2}$ ] used to compare the pyroelectric response of detectors (Whatmore, 1986) suggests that in this respect poly(BTFMND) with a value of  $118 \mu\text{C m}^{-2} \text{K}^{-1}$  at  $20^\circ\text{C}$  is better than PVDF [ $F_D \approx 64 \mu\text{C m}^{-2} \text{K}^{-1}$ ; data taken at 1.69 Hz from Davies (1981)]. For the *cis* poly(BTFMND), the low  $\epsilon_R$  of 5.7 does not allow the attainment of high  $\gamma$  or  $P$  at moderate fields.

### 3.5.3 Stereoblock Fluorocopolymers

Living chain growth polymerization allows the possibility of making block copolymers, which in turn can allow control of the supramolecular organization via the phase separation of incompatible blocks (Woodward, 1988). Blocks derived from the same monomer, but having different microstructures may be incompatible, leading to the possibility of morphology control and hence bulk property control in a material derived from one monomer; such stereoblock copolymers have been prepared via anionic (Poshyachinda et al., 1991) and metallocene (Coates and Waymouth, 1995) methods.

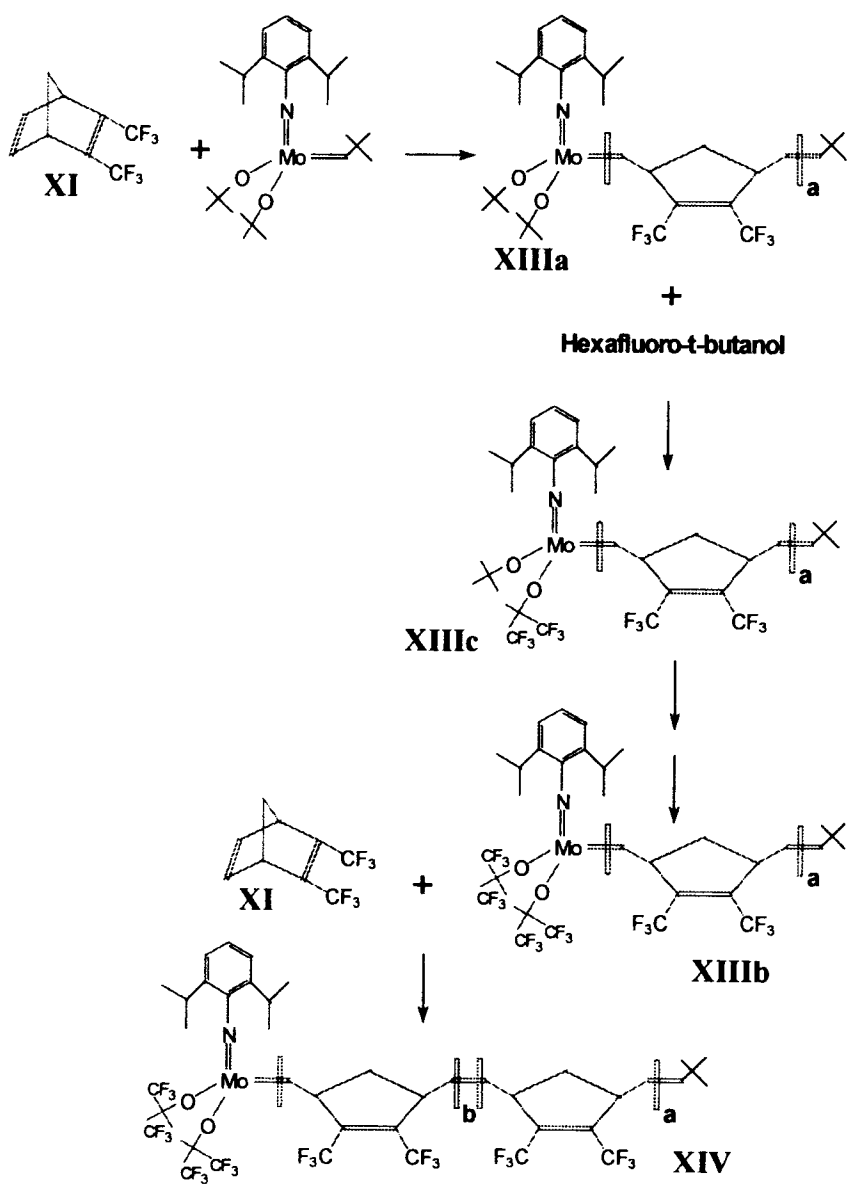
It has been demonstrated that this is also possible using ROMP (Broeders et al., 1996). Poly(BTFMND) has been synthesized as a stereoblock copolymer containing *cis* and *trans* vinylene blocks via ligand exchange in living stereoselective ROMP initiated by a well-defined Schrock-type initiator.

In NMR tube experiments, initiation of **XI** (10 equivalents) with well-defined Schrock molybdenum initiator (see Scheme 3-5) gave polymer **XIIIa** with a living chain end characterized by a doublet in  $^1\text{H}$  NMR (Varian VXR 400,  $\text{C}_6\text{D}_6$  solution) at 11.34 ppm, arising from the alkylidene bound to molybdenum. The solution was

freeze-dried, the residue treated with a solution of dry hexafluoro-*t*-butanol in dry  $\text{C}_6\text{D}_6$  for 30 min, freeze-dried, and the residue redissolved in  $\text{C}_6\text{D}_6$  before recording the spectrum. Three new alkylidene doublets appeared in the spectrum. On the basis of earlier work, the doublet at 12.42 ppm was assigned to the chain end alkylidene **XIIIb** carrying two hexafluoro-*t*-butoxy ligands. The doublets at 11.86 and 11.92 ppm arise from the alkylidene of structure **XIIIc**, in which the molybdenum carries one *t*-butoxy and one hexafluoro-*t*-butoxy ligand and is therefore a chiral center; since the tertiary carbon adjacent to the alkylidene is also chiral, the alkylidene hydrogen may be located between centers of the same or different chirality, giving rise to diastereomeric environments which occur at different chemical shifts and in different abundances. A further four repetitions of this reaction sequence gave the product **XIIIb**, in which all the alkoxy ligands are hexfluoro-*t*-butyl; this was used to initiate the polymerization of **XI** (15 equivalents). The resulting living stereoblock copolymer **XIV** was terminated by the addition of benzaldehyde (10 equivalents) to give a polymer which displayed all the signals associated with *cis* and *trans* vinylene sequences in blocks of poly-(BTFMND). The process was repeated on a larger scale ( $2 \times 100$  equivalents of **XI**) and with the addition of THF to improve polymer solubility, to give a stereoblock copolymer having  $M_n = 73\,000$  (Theoretical 46 000) and  $M_w/M_n = 1.16$  (Viscotek differential refractometer/viscometer, PLgel mixed column, THF, polystyrene calibration). The relatively narrow polydispersity observed is as expected for the product of a well-defined living polymerization process.

The *cis/trans* blocks in the stereoblock copolymer are expected to have the same tacticity as their corresponding homopolymers, as shown in Fig. 3-36.





Scheme 3-5.

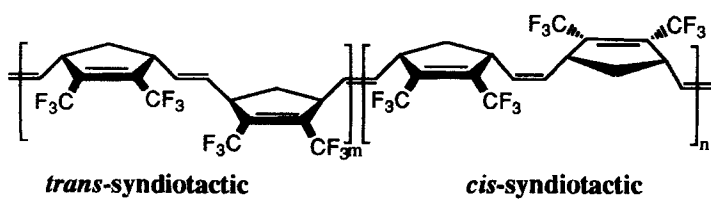


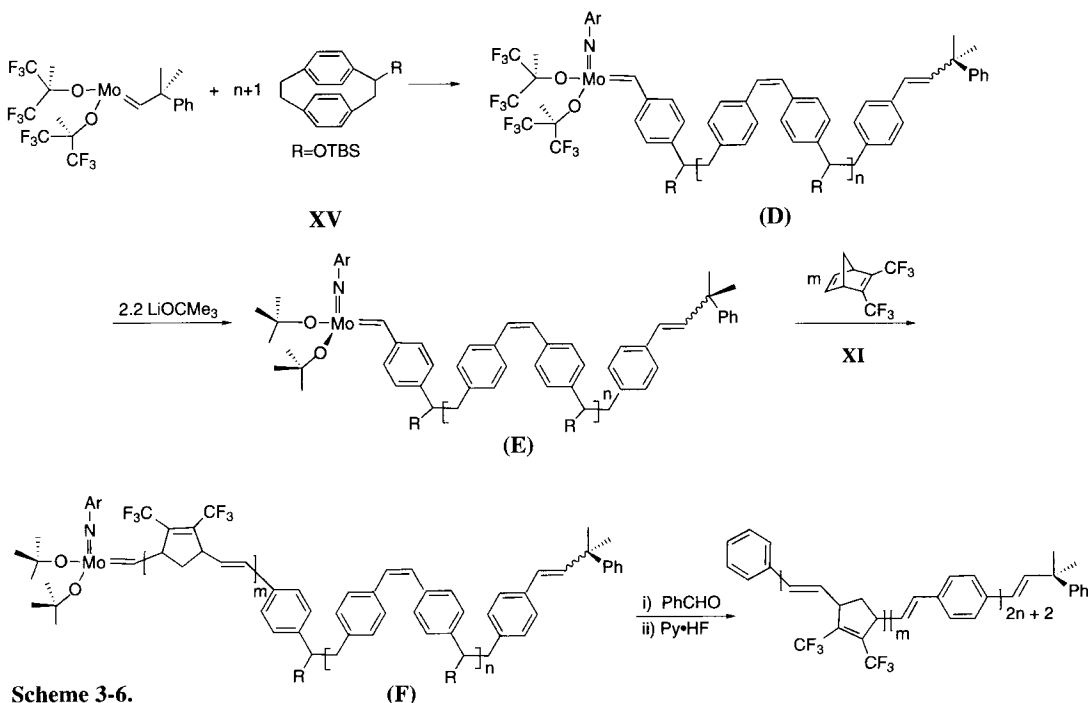
Figure 3-36.

Differential scanning calorimetry (Perkin Elmer DSC7) revealed two transitions at ca. 95 °C and 145 °C, as expected for the *trans* and *cis* blocks, respectively.

### 3.5.4 Synthesis of Electroluminescence Materials

Encapsulation of emissive polymers within a fluorinated matrix using the alkoxide-ligand exchange strategy similar to Sec. 3.5.3 has recently been reported (Bazan et al., 1996). The report involves the synthesis of block copolymers containing poly(*p*-phenylenevinylene) (PPV) and *trans*-syndiotactic-poly(BTFMND). PPV exhibits emissive electroluminescence and can be implemented as an emissive material in high-emitting diodes (Burroughes et al., 1990). The fluorinated section has been shown to have, after poling, a high re-

laxed dielectric constant and demonstrate pyroelectric behavior (Davies et al., 1995). Both homopolymers are accessible via ROMP, but require different molybdenum-based Schrock-type initiators (Schrock, 1990b, 1994). PPV is derived from the *cis*-specific living ROMP of **XV**, which works only when very active initiators, such as molybdenum hexafluoro alkylidene, are used (Miao and Bazan, 1994a, b). Poly-(BTFMND) requires an all-*trans*, highly tactic stereochemistry to maximize its pyroelectric properties (Davies et al., 1995), which is achieved by the less reactive molybdenum *t*-butoxide alkylidene initiator. The detailed sequence of steps is shown in Scheme 3-6. Adding **XV** to the hexafluoro molybdenum initiator results in living *cis*-poly**XV** (**D** in Scheme 3-6). At this stage, 3–4 equivalents of LiOCMe<sub>3</sub> are added, which completely replace their fluorinated counterparts on molybdenum to generate a



Scheme 3-6.

new propagating species **E**. The addition of **XI** to the reaction mixture results in poly**XI**-block-poly**XV** (**F** in Scheme 3-6).

### 3.5.5 Fluorinated Block Copolymers

The ill-defined classical initiator systems are generally unsuited to the preparation of block copolymers. In contrast, the well-defined initiators are capable of producing fluorinated block copolymers in a living manner by the sequential addition of monomers (Feast et al., 1994b). The advantage of these systems, illustrated in Fig. 3-37, is that the complete course of the copolymerization reactions can be followed by  $^1\text{H}$  NMR. When the first monomer is polymerized, characteristic propagating alkylidene resonances are seen in the  $^1\text{H}$  NMR spectrum. When the comonomer is added, after complete polymerization of the first monomer, a new propagating alkylidene signal typical of the second monomer appears. In other words, the propagating alkylidene of the living polymer derived from the first monomer can function as an initiator for the ROMP of the second monomer. This is an obvious requirement for a successful living block copolymerization system, and has been shown

to be the case in similar experiments with a range of fluorinated norbornenes and norbornadienes.

GPC analysis on the block copolymer samples revealed that the samples exhibit narrow molecular weight distributions. Some of the fluorinated block copolymers show two glass transition temperatures which are well-defined; this observation has been confirmed by thermally stimulated current (TSC) studies. This provides clear evidence that the two components are not compatible.

### 3.5.6 Graft Copolymers

The potential of combining the capabilities of living anionic and ROM polymerization methods has been explored to prepare polymers with well-defined structures and unusual topologies. This approach offers access to a range of graft copolymers that can not be prepared by grafting "onto or from" homopolymer backbones. Additionally and importantly, the method allows rational design and synthesis of graft copolymers with control over the main chain and graft-chain molecular weights and the graft density.

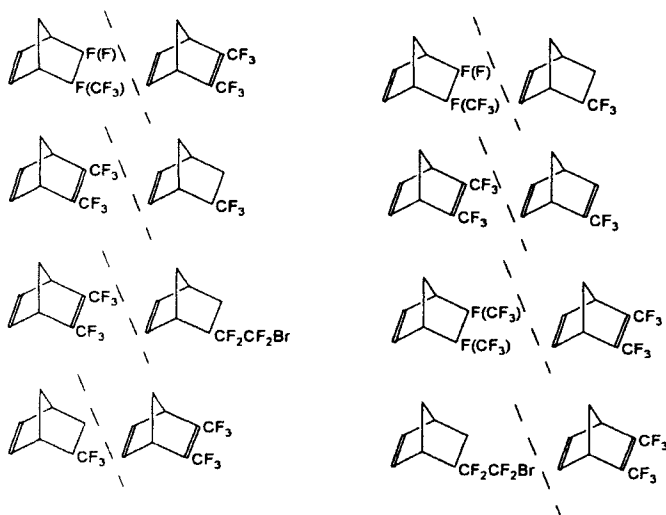
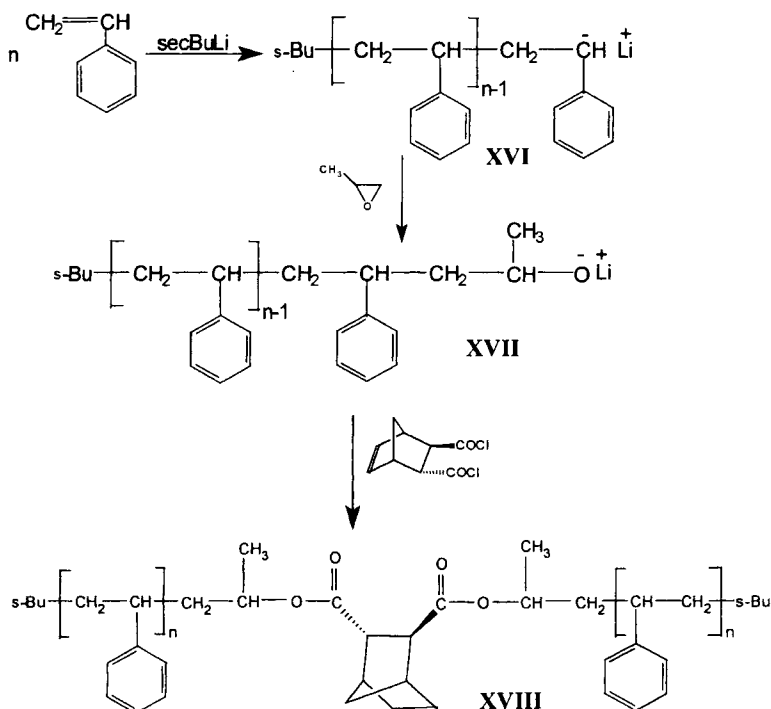


Figure 3-37.

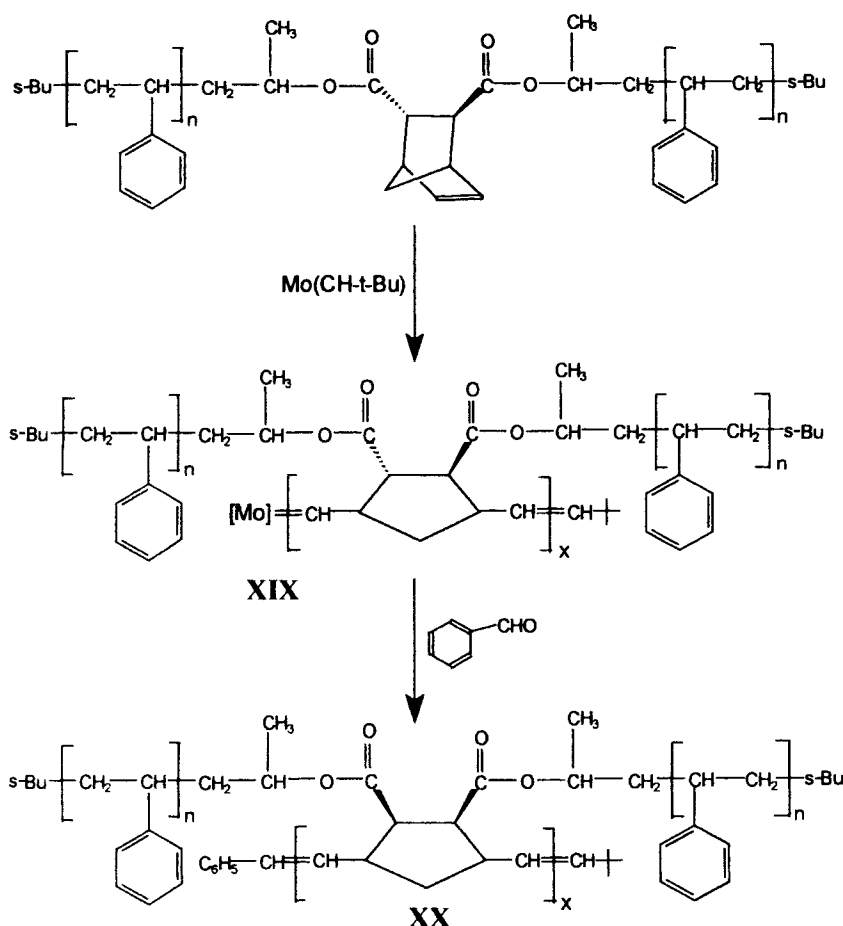
The preparation of polystyrene macromonomers containing a norbornene unit and their living ring opening metathesis polymerization (ROMP) using Schrock initiator to produce well-defined comb graft copolymers has recently been reported (Feast et al., 1994c). Bicyclo[2.2.1]hept-5-ene-2,3-*trans*-bis(polystyrylcarboxylate)s macromonomers (**XVIII**) have been synthesized according to Scheme 3-7.

Macromonomers (**XVIII**) have been subjected to ROMP (Scheme 3-8) to give a polynorbornene derivative carrying two polystyrene grafts on each cyclopentane ring in the polymer backbone (**XX**). Well-characterized macromonomers and comb graft copolymers with polystyryl grafts with average degrees of polymerization (DPs) of 4, 7, and 9 were successfully produced. The graft copolymers exhibit single mode molecular weight distributions and narrow polydispersities.

The scaling up of the ROMP of the macromonomers of different molecular weights, i.e., different polystyrene graft lengths, revealed the presence of a limit on the attainable length of the polynorbornene backbone chain in the graft copolymer, in addition to the limit on the length of polystyrene graft in the macromonomer (Feast et al., 1997). The results indicated that the ROMP of macromonomers with different polystyrene graft lengths go to completion only up to a certain molar ratio of macromonomer to initiator, and in these cases the graft copolymers obtained exhibited single mode molecular weight distributions. However, when the molar ratio of macromonomer to initiator is greater than a threshold value, two peaks appear in the GPC. The lower molecular weight peaks are narrow and, in each case, have the same retention volume as the starting macromonomers; the higher molecular weight peaks also have narrow molec-



Scheme 3-7.



Scheme 3-8.

ular weight distribution and are due to the product graft copolymer. These results suggested that the graft copolymer backbone chain grows up to a certain length beyond which the metathesis polymerization reaction becomes sterically hindered and eventually stops. It appears that as the length of polystyrene graft in the macromonomer is increased the length of polynorbornene backbone chain in the graft copolymer is decreased.

The polymerization reactions are demonstrated to be living by producing block and tapered copolymers with BTFMND monomer (Feast et al., 1997).

Recent work on the synthesis of graft copolymers with a polynorbornene backbone

chain carrying one polystyrene graft in each cyclopentene ring revealed that, in contrast to the case discussed above, higher molecular weight graft copolymers can be prepared (Rizmi, 1997). Pure *exo*-5-norbornene-2-(polystyrylcarboxylate) macromonomers were prepared and polymerized following Scheme 3-7 and 3-8.  $^1\text{H}$  NMR spectra of living reaction mixtures showed two broad propagating alkylidene signals which were attributed to head and tail insertion of macromonomer repeat units in the polymer chain. The intensity of these two alkylidene signals are approximately the same, indicating that the graft copolymer contains 50:50 head-tail placement of repeat units, which results in reduced steric

congestion and hence allows increased molecular weights of these graft copolymers to be attained.

Breunig et al. (1995) have synthesized graft copolymers in a similar manner using *exo/endo*-5-norbornene-2-(polystyrylcarboxylate) macromonomers and Schrock hexafluoro molybdenum initiator. The graft copolymers are reported to be difficult to hydrogenate due to the presence of ester groups (Heroguez et al., 1996 a). In another approach, 5-methylene lithium norbornene was synthesized and used as an initiator for the anionic polymerization of styrene to produce ring open polymerizable macromonomers with no ester linkages (Heroguez et al., 1996 a). Macromonomer with  $M_n = 2600$ , synthesized by this method, was subjected to ROMP using the hexafluoro molybdenum alkylidene initiator, and the polymerization was shown to go to completion.

Synthesis of 5-norbornene-2-(polyethylene oxide) macromonomers and their ROMP has also been reported (Heroguez et al., 1996 b). The potassium alkoxide of 5-hydroxymethyl norbornene has been used as an initiator for the anionic polymerization of ethylene oxide and the resulting macromonomers were polymerized using the hexafluoro molybdenum alkylidene initiator.

### 3.5.7 Nanoscale Clusters via Microphase-Separated Materials

Schrock has shown that the molybdenum and tungsten catalysts can tolerate main group and transition metal functionalities appended to the norbornene skeleton, and has exploited these monomers to prepare low dispersity block copolymers with well-defined microphase-separated regions (Cummins et al., 1991, 1992; Sankaran et al., 1990, 1991; Ng Cheong Chan and

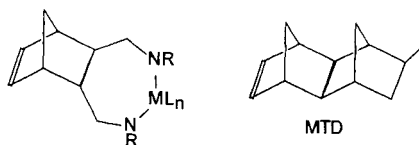


Figure 3-38.

Schrock, 1993; Ng Cheong Chan et al., 1992 a, b). A type of monomer that has proved particularly effective for carrying metals into microphase-separated materials is the chelating diamide substituted norbornenes (Cummins et al., 1991, 1992) illustrated in Fig. 3-38.

The morphologies of these copolymers were investigated by transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS).

Depending on the ratio of norbornene to metal-derivatized bis-amide, materials containing lamellae, cylinders, or spheres of the metal-containing component embedded in polynorbornene can be obtained. For the purpose of film-forming and microtoming of samples, the higher  $T_g$  polymer arising from methyltetracyclododecene (MTD) was found to be superior to polynorbornene (Ng Cheong Chan et al., 1992 b). The microphase-separated polymers can then be chemically treated to give aggregates of, for example, semiconductor materials such as ZnS and CdS (Cummins et al., 1992), and nanoclusters of metallic palladium or platinum (Ng Cheong Chan et al., 1992 a), silver or gold (Ng Cheong Chan et al., 1992 b).

### 3.5.8 Side Chain Liquid Crystal Polymers

In recent years, considerable effort has been directed to the synthesis of novel side chain liquid crystalline polymers because of a variety of applications, especially in the field of electrooptics (Finkelmann et al.,

1983; Coles and Simon, 1985). Side chain liquid crystallinity generally requires a molecular structure in which a flexible polymer chain, or a flexible connector group between the mesogen and backbone, provides sufficient conformational freedom to allow the rigid mesogenic units to form stacks or organized domains (Finkelmann et al., 1978 a, b). Side chain liquid crystalline polymers (SCLCPs) have been prepared mainly by radical polymerization of mesogenic acrylates and methacrylates. Because it is difficult to control both the molecular weight and the polydispersity of the resulting polymers, it is of limited use for determining the influence of molecular weight distribution on the phase behaviour of SCLCPs (Percec and Pugh, 1989).

Living polymerization methods allow synthesis of polymers with well-defined structures (Grubbs and Tumas, 1989; Schrock, 1990 a; Rempp and Merrill, 1986; Webster, 1991). Although anionic polymerization has been exploited the most, the living nature of the system is often impeded by the presence of polar substituents on the monomer (Nakamura and Hirao, 1990). More recent advances have witnessed the use of living ROMP in the synthesis of SCLCPs (Komiya et al., 1992 a, b; Pugh and

Schrock, 1992; Komiya and Schrock, 1993 a, b; Ungerank et al., 1995). Schrock and co-workers have recently reported the living ROMP of mesogenic norbornene derivatives using  $\text{Mo}(\text{CH-}t\text{-Bu})(\text{NAr})(\text{O-}t\text{-Bu})_2$  as the initiator (Fig. 3-39) and described the influence of spacer length, molecular weight, and molecular weight distribution on the phase behavior of the resulting polymers (Komiya et al., 1992 a; Komiya and Schrock, 1993 b). The transitions become independent of molecular weight when the chains contain 30–40 repeat units or more, and polymers with an odd number of methylene units in the spacer display a higher transition temperature than those with an even number. This alternation vanishes when the spacer length is greater than six. All the polymers prepared exhibited an enantiotropic nematic mesophase.

Diblock copolymers having well-defined block lengths often produce microphase-separated morphologies (lamellae, cylinders, or spheres) in cast films. If one of the blocks is an SCLCP, then a liquid crystalline (LC) microphase would be expected to form within one of the microdomains. This has been demonstrated in the synthesis of AB type block copolymers that contain an

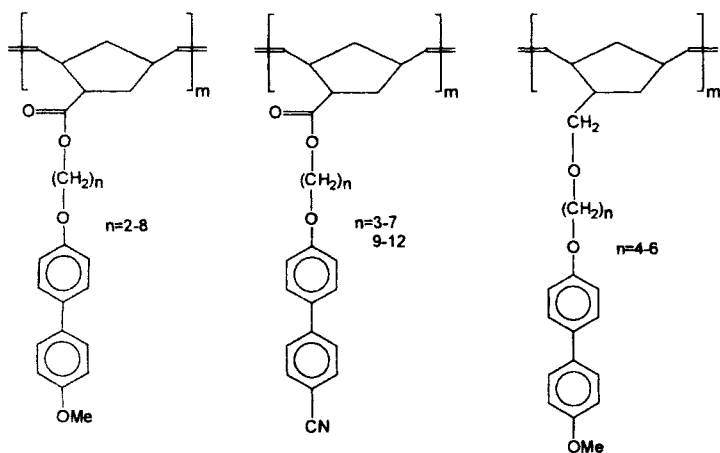


Figure 3-39.

SCLCP block and an amorphous polymer block by employing living ROMP. Norbornene, 5-cyano-2-norbornene, and methyl-tetracyclododecene were used for the amorphous polymer blocks, and  $n$  {[ (4'-methoxy-4-biphenyl)yl]oxy}alkyl bicyclo [2.2.1]hept-2-ene-5-carboxylates (Fig. 3-40) were used for the SCLCP block (Komiya and Schrock, 1993 a).

Norbornene derivatives containing laterally attached 2,5-bis[(4'- $n$ -alkoxybenzoyl)oxy] mesogens (Fig. 3-41) were polymerized by controlled ROMP to provide

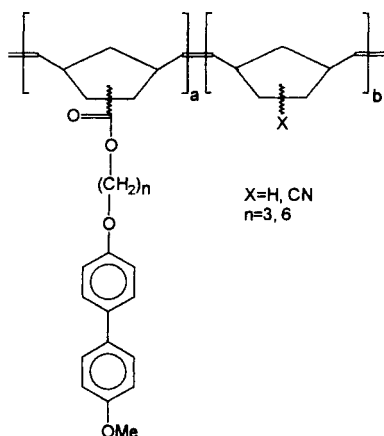


Figure 3-40.

polymers in a high yield with 5–100 repeat units and narrow molecular weight distributions (Pugh and Schrock, 1992). All the polymers displayed enantiotropic nematic mesophases regardless of the spacer, molecular weight, or length of the  $n$ -alkoxy substituent.

The SCLCPs described above contain just one pendant mesogenic group per norbornene repeat unit. Stelzer and co-workers (Ungerand et al., 1995) have prepared SCLCPs with two pendant mesogenic groups per norbornene repeat unit (Fig. 3-42). They studied the effect of spacer length on the isotropization temperature. The polymers are reported to be glassy with no side chain crystallization occurring. Polymers also show an odd-even effect which is very clear for nematic polymers with a spacer length of 2 to 7, while quite vague for smectic polymers with a spacer length of 8 to 12.

Discotic liquid crystalline polymers bearing alkoxy-substituted triphenylene moieties in the side chain have been synthesized by ROMP using a well-defined ruthenium initiator (Weck et al., 1997).

To elucidate the effect of backbone flexibility on the mesomorphism, norbornene (**XXIa–b**, Scheme 3-9) and cyclobutene

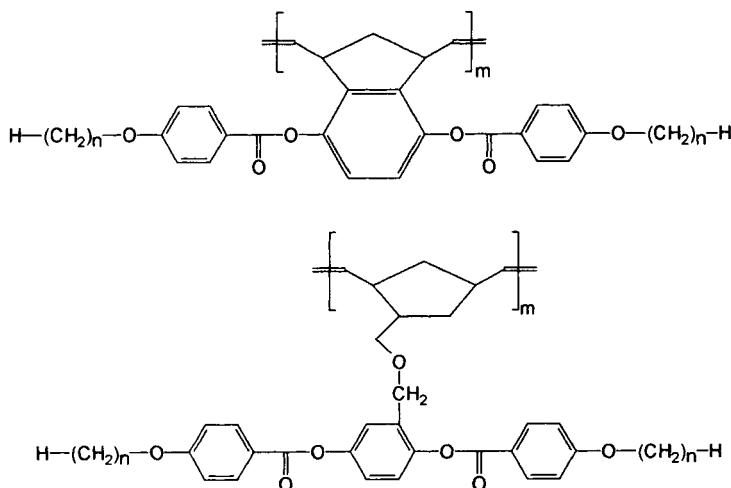


Figure 3-41.



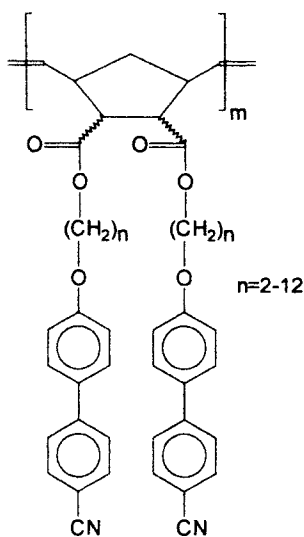


Figure 3-42.

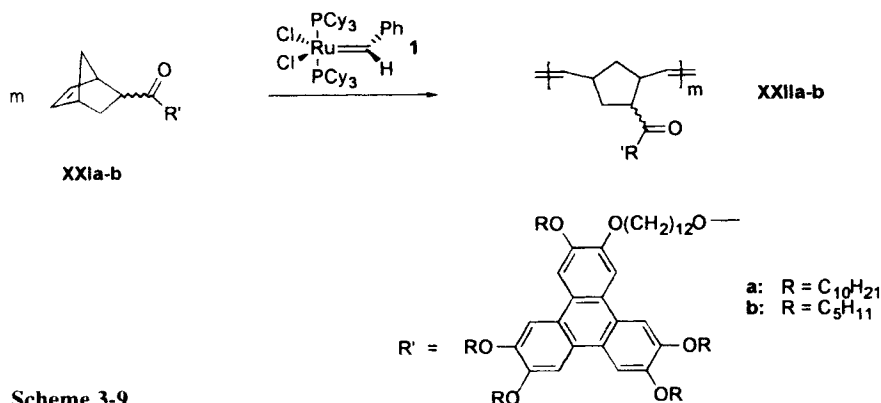
(XXIIIa–b, Scheme 3-10) monomers containing triphenylene moieties have also been synthesized, which yielded the relatively rigid poly(norbornene)s (XXIIa–b, Scheme 3-9) and the more flexible poly(butadiene)s (XXIVa–b, Scheme 3-10), respectively, after polymerization.

To further increase the backbone flexibility, the poly(butadiene)s (XXIVa–b, Scheme 3-11) were hydrogenated using Crabtree's catalyst to yield triphenylene-substituted poly(1,4-butylene)s (XXV a–b, Scheme 3-11). The mesomorphic behavior of the polymers has been investigated by

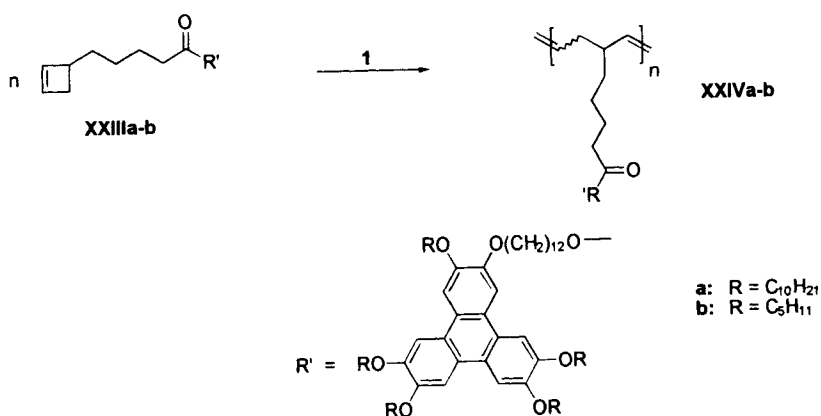
DSC and powder diffraction X-ray scattering (wide-angle X-ray scattering, WAXS). All polymers bearing a 2,3,6,7,19-decyloxy-triphenylene based mesogenic unit exhibited enantiotropic discotic hexagonal mesophases, while the pentoxy analogs did not display liquid-crystalline behavior. No effect of backbone rigidity on the mesomorphism could be detected.

The effect of backbone flexibility on the mesomorphic behavior of side chain liquid crystalline polymers synthesized by ring-opening metathesis polymerization have recently been investigated (Maughon et al., 1997). The synthesis of norbornene (XXVIa–d, Scheme 3-12) and cyclobutene (XXVIIIa–d, Scheme 3-13) monomers containing a *p*-nitrostilbene moiety as the mesogenic group, and polymerization of these monomers to produce side chain liquid crystalline polymers with low polydispersities and defined molecular weights have been accomplished.

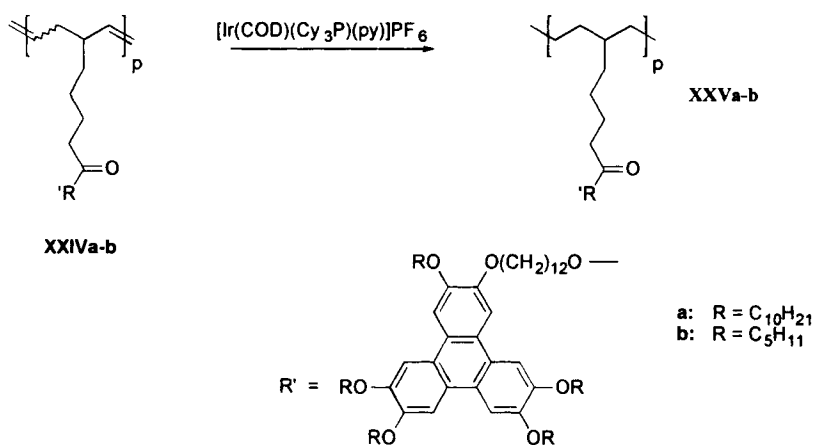
The relatively rigid poly(norbornene)s (XXVIIa–d, Scheme 3-12) displayed enantiotropic nematic mesomorphism with glass transitions from 44 to 64 °C and isotropization temperatures between 108 and 121 °C, whereas the more flexible poly(butadiene)s (XXIXa–d, Scheme 3-13) showed enantiotropic smectic A mesomorphism with



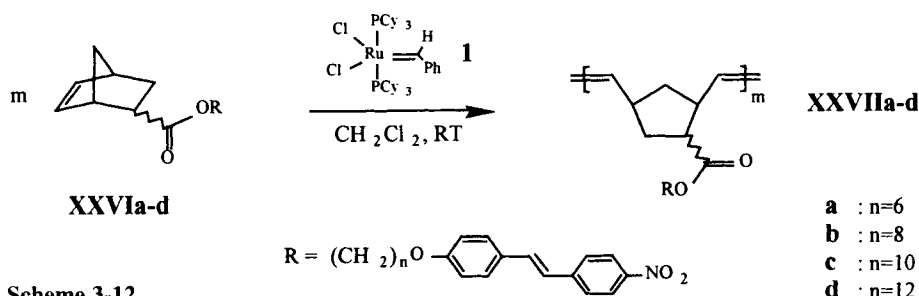
Scheme 3-9.



Scheme 3-10.



Scheme 3-11.

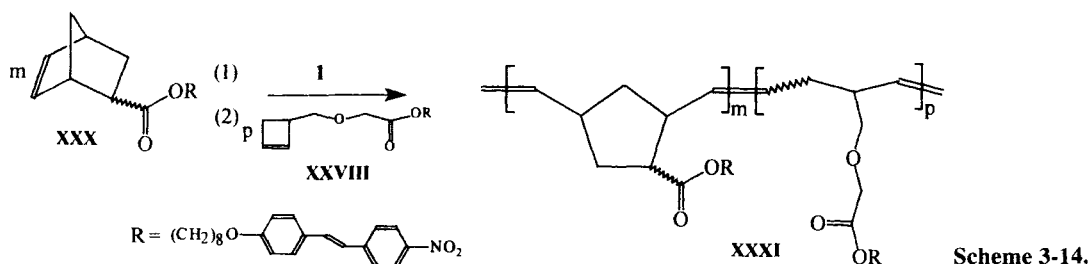
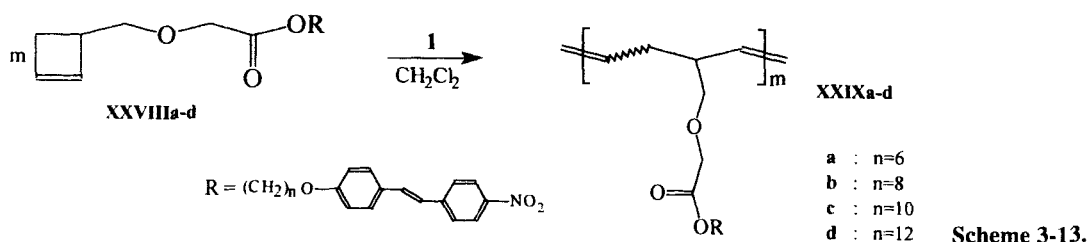


Scheme 3-12.

glass transition temperatures from 14 to 31 °C and isotropization temperatures between 74 and 111 °C.

Surprisingly, a diblock copolymer containing a 1:1 mixture of the poly(norbornene) and poly(butadiene) (**XXXI**, Scheme 3-14) also exhibited the more or-

dered smectic A mesophase. The dependence of the degree of polymerization and flexible spacer length on the phase transitions of these systems was determined, demonstrating stabilization of the mesophase by both increasing the molecular weight and the flexible spacer length.



### 3.5.9 ABA Triblock Copolymers

Norbornene and 7-oxanorbornene derivatives have been polymerized by ROMP in a living manner by employing three new well-defined, bimetallic ruthenium catalysts  $(\text{PR}_3)_2\text{Cl}_2\text{Ru}(\text{=CH-}p\text{-C}_6\text{H}_4\text{-C(H)=})\text{-RuCl}_2(\text{PR}_3)_2$  (**XXXIIa-c**, Fig. 3-43) as initiators to obtain ABA triblock copolymers with low polydispersities (Weck et al., 1996).

Reactions of 7-oxanorbornenes **XXXIII** and **XXXIV** or a silicon-containing norbornene **XXXV** (Fig. 3-44) with **XXXIIc** resulted in polymers with low polydispersities ranging from 1.10 to 1.19, while polymerizations initiated by **XXXIIb** displayed higher polydispersities ranging from 1.20 to 1.35. The polymerizations catalyzed by **XXXIIb** and **XXXIIc** fulfill the requirements for a living polymerization. However, catalyst **XXXIIa** is not reactive enough to polymerize functionalized norbornenes or 7-oxanorbornenes. The living polymerizations were successfully used to prepare three ABA triblock copolymers of

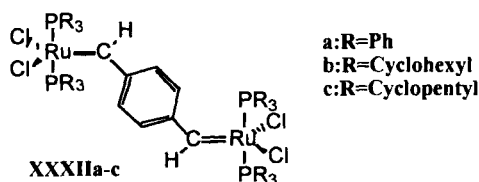


Figure 3-43.

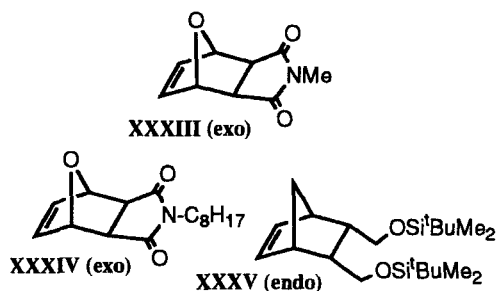


Figure 3-44.

monomers shown in Fig. 3-44. In all cases, these ABA triblock copolymers have higher molecular weights than the homopolymers, and all the polydispersities remained low.

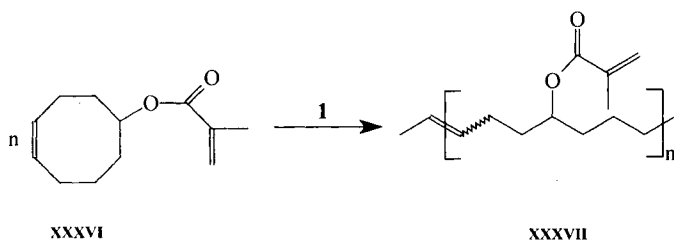


Figure 3-45.

### 3.5.10 Synthesis of AB Cross-Linked Materials

The ROMP of 5-methacryloyl-1-cyclooctene, **XXXVI**, to produce a linear polymer, **XXXVII**, with methacrylate side chains using initiator **1** (ruthenium initiator shown in Fig. 3-5) has been demonstrated (Maugon and Grubbs, 1996). The copolymerization of this monomer with cyclooctadiene allowed for the incorporation of a varying number of methacrylate side chains on the polymer backbone (Fig. 3-45). These polymers were cross-linked through the methacrylate side chains with either thermal or photochemical initiation. A comparison of the physical properties of PMMA and these AB cross-linked materials demonstrated that these materials had higher thermal stability and solvent resistance than pure PMMA.

## 3.6 Conclusion

As demonstrated above, recent developments in olefin metathesis have overcome many of the impediments associated with the earlier catalyst systems. The control of structure and functional group (impurity) tolerance of the new system suggest that the early promise of olefin metathesis can now be realized.

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## 4 Acyclic Diene Metathesis (ADMET) Polymerization

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## List of Symbols and Abbreviations

$n$	number
$p$	extent of reaction
$X_n$	degree of polymerization
Ac	acetyl
ADMET	acyclic diene metathesis
Bu	butyl
Cy	cyclohexyl
Et	ethyl
Me	methyl
NMR	nuclear magnetic resonance
Ph	phenyl
Pr	propyl
py	pyridine
ROMP	ring opening metathesis polymerization
tol	toluene

## 4.1 Introduction

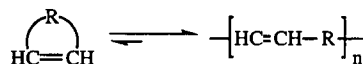
The olefin metathesis reaction, which has been studied for more than 40 years, continues to intrigue chemists with respect to the many new molecules that can be synthesized using this technique. The word metathesis originates from the Greek “meta” meaning change and “tithemi” meaning place. The term was first applied in an organic chemical sense by Calderon et al. (1967) to describe the interchange of two olefins by the movement of bonding electrons to form two new olefins.

The success of olefin metathesis as a synthetic tool can be attributed to outstanding advances in the fields of catalysis and organometallic chemistry. The reaction has prompted intense mechanistic investigations to explain how catalysts are able to accomplish this transformation at room temperature, and much is known today with respect to the nature of this chemistry. While the reaction is employed both in the synthesis of small molecules and in the preparation of polymers, this chapter only deals with the utilization of olefin metathesis in condensation polymerization chemistry.

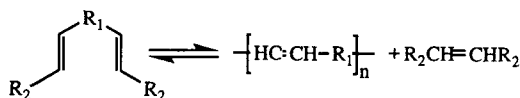
Two types of metathesis polymerizations have been defined to date, as illustrated in Fig. 4-1. Ring opening metathesis polymerization (ROMP) is a chain polymerization process which generates high molecular weight polymers by exposing strained cyclic olefins to an appropriate catalyst. The reaction was known as far back as the 1950s [Eleuterio, 1963 (filed 1957)], and is used commercially today to produce specialty polymers such as polynorbornene and polydicyclopentadiene. The ROMP reaction has long dominated the field of metathesis polymerization, and is discussed in detail in Chap. 3 of this Supplement.

A more recent approach to producing generically the same type of repeat unit is al-

### Ring Opening Metathesis Polymerization (ROMP)



### Acyclic Diene Metathesis (ADMET) Polymerization



**Figure 4-1.** Ring opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) polymerization.

so shown in Fig. 4-1. Acyclic diene metathesis (ADMET) is step polymerization chemistry which occurs by way of a condensation reaction to produce high molecular weight polymers. Opportunities here have begun to unfold over the past decade, and it now is evident that the ADMET reaction has the potential to join ROMP polymerization as a method of generating high molecular weight molecules.

## 4.2 Catalysts in Acyclic Diene Metathesis (ADMET) Chemistry

### 4.2.1 Classical Catalysts

Classical metathesis catalysts, as shown in Table 4-1, are typically composed of a transition metal halide and a nontransition metal cocatalyst, which form a metathesis active alkylidene in situ. These systems tend to be ill-defined, since the true active catalyst in the system is not known, and further, the presence of a Lewis acid cocatalyst can lead to side reactions which compete with metathesis polymerization. Although they are ill-defined, classical catalysts find favor in industrial processes as they are relatively inexpensive to use.

**Table 4-1.** Representative classical catalyst systems for metathesis polymerization.

Catalyst system	Solvent/ temp. (°C)	References
MoCl <sub>2</sub> (NO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> /Me <sub>2</sub> Al <sub>2</sub> Cl <sub>3</sub>	chlorobenzene/25	(Grubbs et al., 1976; Zuech et al., 1970)
Bu <sub>4</sub> N [Mo(CO) <sub>5</sub> COPh]/MeAlCl <sub>2</sub>	chlorobenzene/20	(Kroll and Doyle, 1971)
(py)Mo(CO) <sub>5</sub> /EtAlCl <sub>2</sub> /NBu <sub>4</sub> Cl	chlorobenzene/20	(Farona and Motz, 1976; Motz and Farona, 1977)
(tol)W(CO) <sub>3</sub>	heptane/98	(Lewandos and Pettit, 1971)
WCl <sub>4</sub> /BuLi	benzene/20	(Grubbs et al., 1975)
PhWCl <sub>3</sub> /AlCl <sub>3</sub>	chlorobenzene/20	(Grubbs et al., 1975)
ReCl(CO) <sub>5</sub> /EtAlCl <sub>2</sub>	chlorobenzene/90	(Farona and Greenlee, 1975)

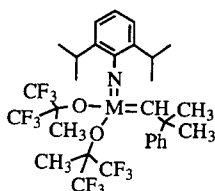
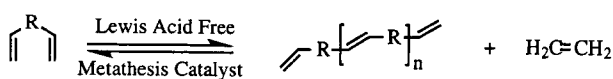
Classical catalysts can be employed quite successfully in the production of ROMP polymers, yet appear to be considerably less useful for ADMET polymerization. ROMP reactions are more forgiving in terms of catalyst selection, since they are based on chain polymerization principles. The strict requirements of step growth polymerization chemistry demand precise catalyst structures in order for the ADMET polymerization to proceed to the formation of high polymer. For this reason, early efforts at condensation of acyclic dienes were met with only limited success (Dall'Asta, 1973; Doyle, 1973; Zuech et al., 1970).

More recently, however, classical catalysts have been shown to hold promise for ADMET reactions if the Lewis acidity of the systems is properly addressed. Nubel et al. (1994) demonstrated that the presence of a Lewis base suppresses vinyl addition chemistry, such that macromolecules of number average molecular weight 5000 can be generated by a pure metathesis mechanism. This discovery could lay the foundation for commercial expansion of the ADMET process, since classical catalyst systems offer a great deal of versatility in terms of their breadth and availability.

#### 4.2.2 Well-Defined Catalyst Systems

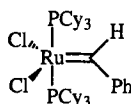
Although olefin metathesis aided by the utilization of classical catalyst systems has been carried out for some time, the advent of well-defined catalysts is a rather recent occurrence. Most of the research that has been conducted to date has been based on using well-defined catalyst structures first reported by Schrock. These alkylidenes are of the form M(NAr)[CHC(CH<sub>3</sub>)<sub>2</sub>Ph][OCCH<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, where M = W (Schrock et al., 1988) or Mo (Schrock et al., 1990), and are illustrated in Fig. 4-2. Since these alkylidenes are known for exclusively catalyzing metathesis chemistry, they have essentially permitted the evolution of ADMET chemistry as it stands today by assuring an exact mode of polymerization, which is required of step propagation.

Recently, other catalyst systems have been shown to be effective in producing high molecular weight ADMET polymers. For example, the ruthenium catalysts reported by Grubbs (Nguyen et al., 1992; Schwab et al., 1995; Schwab et al., 1996) are useful in ADMET reactions and can be distinguished from Schrock systems in that they are more tolerant of polymerization condi-



M = W or Mo

Schrock's Catalyst



Cy = cyclohexyl

Grubbs' Catalyst



Nubel's Catalyst

**Figure 4-2.** Well-defined catalysts systems employed in metathesis polymerization.

tions. These ruthenium alkylidenes can be used in the presence of water and other protic solvents (Nguyen et al., 1992), and require both less rigorous purification of monomers and less rigorous polymerization conditions to produce high molecular weight polymers.

Recent kinetic studies show that the ADMET reaction is second order in monomer, as is expected in step polymerization chemistry, and zero order in catalyst, regardless of the catalyst choice. Reaction rates, however, are completely dependent upon the identity of the catalyst with the Schrock alkylidenes being at least an order of magnitude faster than well-defined ruthenium catalyst systems. Further, the catalyst choice can alter the nature of the competition between propagation (the intermolecular reaction) and cyclization (the intramolecular reaction), particularly for monomers where intramolecular complexation between the metal and an internal olefin can occur in a facile manner.

The proper choice of catalyst is essential for the realization of metathesis polymerization chemistry. For processes such as

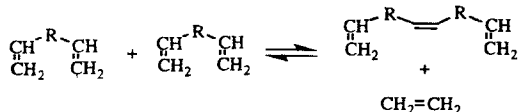
ROMP, where the reaction conditions are not extremely sensitive to impurities, a classical catalyst system can be employed with great success. However, in experiments where a well-defined catalyst with an exact structure is needed, such as acyclic diene metathesis polymerization, a preformed alkylidene which does not require a Lewis acid cocatalyst must be employed.

## 4.3 The Key to ADMET Polymerization

### 4.3.1 The Step Polymerization Nature of ADMET Chemistry

The nature of acyclic diene metathesis chemistry is shown in Fig. 4-3, where the structural changes that occur during the reaction are illustrated. The diene monomers condense to produce an ADMET "dimer", releasing ethylene from the reaction. This is an equilibrium polymerization which can be driven to form high molecular weight polymer by the continuous removal of ethylene under vacuum.

## ADMET Dimerization



## ADMET Polymerization

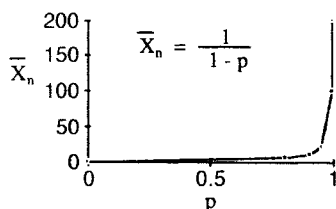
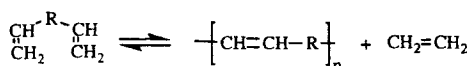


Figure 4-3. The step nature of the ADMET reaction.

Keeping these events in mind, it becomes apparent that acyclic diene metathesis polymerization is a step process, as opposed to the chain polymerization chemistry associated with ROMP reactions. A plot of Carothers' equation (Fig. 4-3) illustrates that in order for high molecular weight polymer to be formed, conversions of functional groups must be essentially quantitative. Even at 99% conversion, the degree of polymerization is only  $X_n=200$ . Without quantitative conversion, step polymerizations are ineffective routes to generate high polymer; the same holds true for ADMET polymerization. In this regard, monomer purity and perfect difunctionality are essential for obtaining high molecular weight polymers.

### 4.3.2 Effects of Lewis Acid Cocatalysts

Attempts were made as early as 1970 to produce ADMET polymers (Dall'Asta, 1973; Doyle, 1973; Zuech et al., 1970),

where experiments to condense 1,5-hexadiene resulted only in the formation of low molecular weight oligomers. More recently, in the late 1980s (Lindmark-Hamberg and Wagener, 1987), attempts were made to condense 1,9-decadiene into polyoctenamer using a classical catalyst system. While the monomer condenses to produce an intractable polymeric product, the reaction is not entirely selective for metathesis chemistry (Fig. 4-4). Rather than constructing a polymer exclusively derived from the metathesis mechanism, other repeat units are generated from a vinyl addition process. The formation of these repeat units can be attributed to the presence of the Lewis acid cocatalyst in the polymerization system, and the consequence of using this type of catalyst is to have two reaction mechanisms competing for the same monomer, thereby leading to an intractable, insoluble product. Thus it becomes evident that competing reactions hinder the progress of the metathesis reaction.

The effect of an acid catalyst on the reaction mechanism has been illustrated by a model compound study (Wagener et al., 1990) to distinguish between competing mechanistic types (Fig. 4-5). The model reagent, styrene, could either experience metathesis chemistry producing stilbene, or undergo vinyl addition polymerization to yield polystyrene. Only polystyrene is gen-

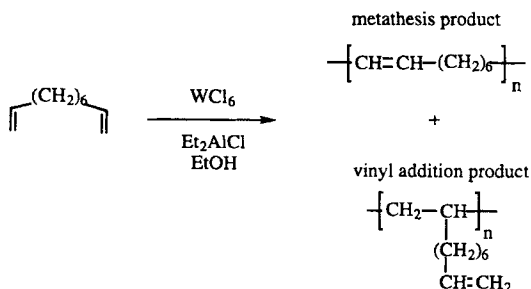
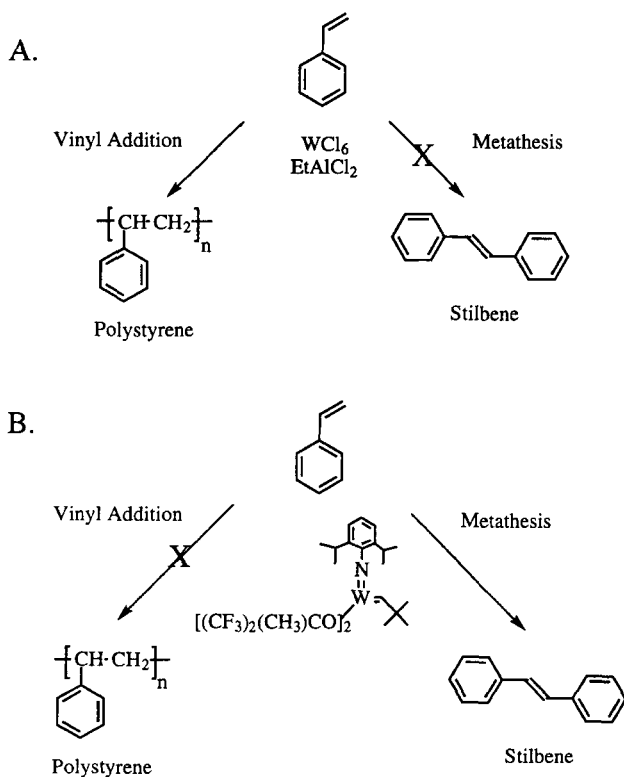


Figure 4-4. The adverse effects of a Lewis acid on metathesis polymerization.



**Figure 4-5.** Styrene model study:  
A. Classical catalyst. B. Well-defined catalyst.

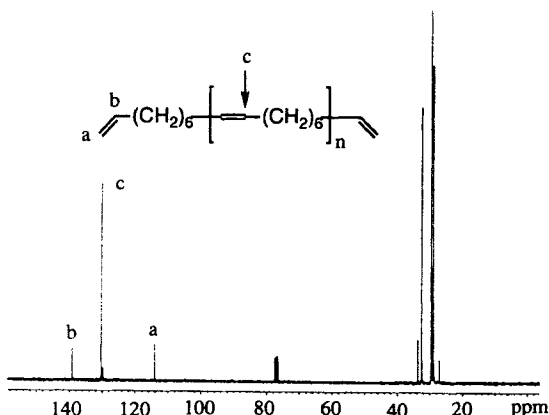
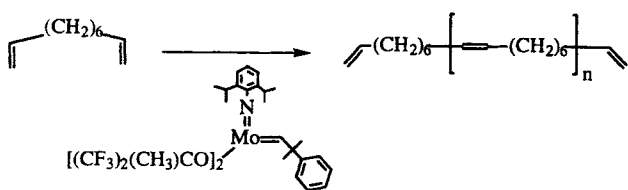
erated in the presence of the classical catalyst system ( $\text{WCl}_6/\text{EtAlCl}_2$ ). However, the mechanistic choice is completely reversed if a well-defined catalyst which does not require a Lewis acid cocatalyst is used, such as Schrock's tungsten alkylidene. This results in clean metathesis chemistry, producing stilbene in quantitative yields. This observation made it clear as to what should be done in order for ADMET polymerization to be successful, i. e., a catalyst system that does not employ a Lewis acid cocatalyst must be chosen in order to avoid competing vinyl addition chemistry.

#### 4.3.3 Synthesis of First High Molecular Weight ADMET Polymers

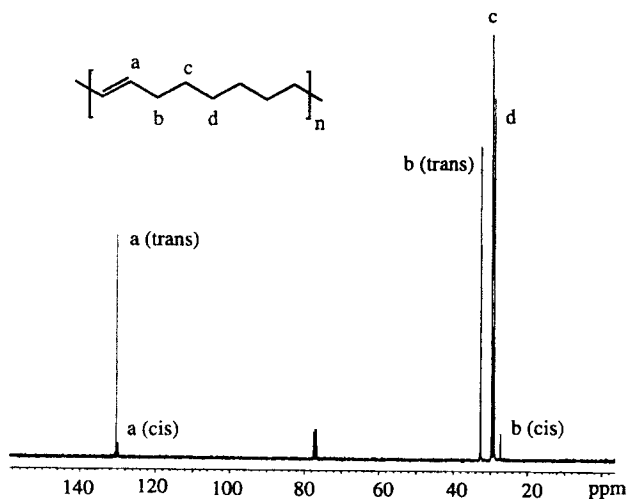
The synthesis of the first high molecular weight polymer by ADMET chemistry was

accomplished by choosing a well-defined alkylidene as an initiator, as suggested in the previous section (Nel et al., 1989). When 1,9-decadiene is exposed to Schrock's molybdenum alkylidene, it is converted to an oligomer via the loss of ethylene under atmospheric pressure. Figure 4-6 illustrates the carbon spectrum of the clean metathesis oligomer, and in this case the  $\text{sp}^2$  region shows only two signals, one for *trans* and the other for *cis* internal olefins present in the repeat unit. The endgroups are also evident in this spectrum, showing that the reaction is quite clean. Further, the  $\text{sp}^3$  region shows only methylene carbons; no methine carbons are present, which would have been created as a result of vinyl addition chemistry.

Vacuum is applied to further remove ethylene and continue the polymerization, and Fig. 4-7 shows the carbon NMR spec-



**Figure 4-6.** The first oligomers by ADMET polymerization.



**Figure 4-7.** Poly(octenylene): The first high molecular weight polymer generated by ADMET condensation.

trum for the first high molecular weight ADMET polymer made by this method (Wagener et al., 1990). The poly(octenylene) that is formed is more than 90% trans as assigned by the  $sp^2$  carbons. It is a pure polymer with an intrinsic viscosity of 0.95 dl/g which correlates to a number average molecular weight of more than 50 000, and has a crystalline melting point of around 70 °C. Fur-

ther, the polymer experiences recrystallization upon cooling. This is a very well-defined macromolecule and is considered to be pure in the sense that only one repeat unit is present. Cyclics are also present, as is typical of any step polymerization, such as in the formation of nylon and polyester (Odian, 1991).

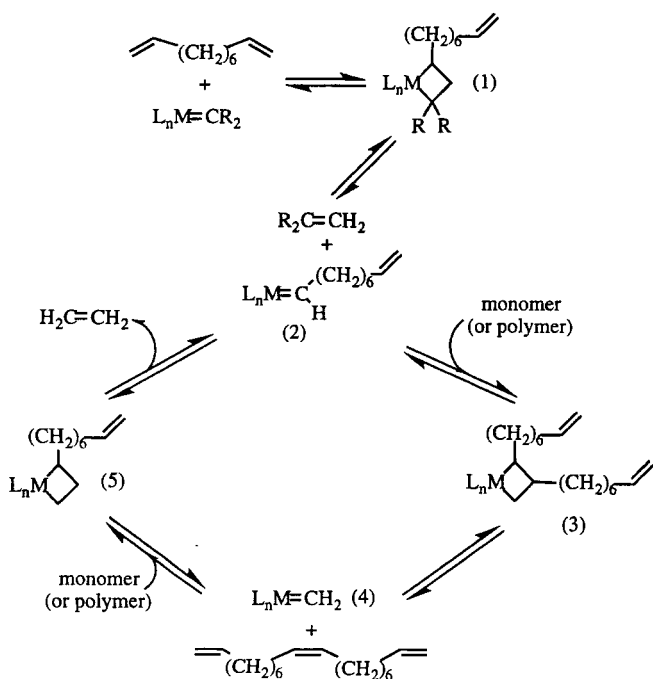
### 4.3.4 The ADMET Polymerization Mechanism

The acyclic diene metathesis polymerization cycle is illustrated in Fig. 4-8. The principal reaction intermediate, a metallacyclobutane, is identical to that found in all other metathesis chemistry, including ring opening metathesis polymerization and the formation of small molecules through metathesis. The ADMET polymerization cycle itself, however, is distinct and quite different from any other reaction scheme found in metathesis chemistry.

Acyclic diene metathesis is an equilibrium process, whereas ROMP typically propagates in an irreversible manner. First, the alkylidene forms a  $\pi$  complex with one of the olefins of the monomer, then the complex undergoes an insertion to form the initial metallacyclobutane (1). This metallacycle can undergo productive metathesis to eliminate a catalyst fragment and form a new alkylidene at the terminus of a

monomer molecule (2). The polymerization cycle then proceeds by complexing this metallized monomer with another monomer unit, forming a new metallacycle (3). Formation of this metallacycle (3) is essential to propagation, and understanding the factors that lead to its formation is important in the elucidation of what type of monomers can be used in ADMET polymerization. This new metallacyclobutane (3) collapses to form an ADMET "dimer" and a methylene alkylidene (4), the latter of which is the true catalyst for this system. The methylene alkylidene continues the cycle by reacting with another monomer (or polymer chain end) to form metallacycle (5), which is the precursor to the formation of ethylene.

Thus the cycle is complete – the consequence being the condensation of two monomer units. The cycle must operate many times in order to produce a high molecular weight polymer by ADMET chemistry. This mechanism has proven to be acceptable in explaining all experimental ob-



**Figure 4-8.** The ADMET polymerization cycle.



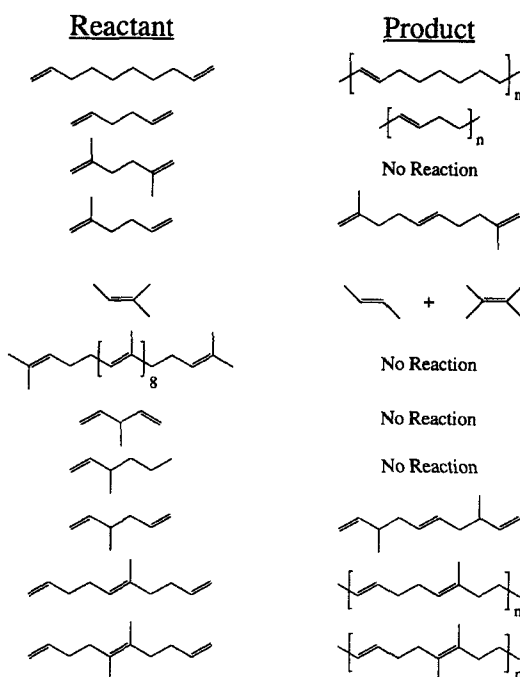
servations made for both pure hydrocarbon monomers, as well as those that possess functional groups.

## 4.4 Hydrocarbons in ADMET Chemistry

### 4.4.1 Nonconjugated Dienes

Determining the type of diene that is capable of ADMET polymerization has been accomplished by systematically examining the effect of substituents and functional groups on the polymerization mechanism described in the previous section. In the case of nonconjugated dienes, substituent effects were examined using methyl groups located at appropriate places in the monomer backbone (Fig. 4-9). For example, 1,5-hexadiene polymerizes easily, as does 2,6-octadiene (Konzelman and Wagener, 1992), where in both cases 1,4-polybutadiene is generated. However, if the methyl groups are moved to the internal carbon of the metathesizing olefin, then the reaction is completely stopped. For example, 2,5-dimethyl-1,5-hexadiene is completely inert to ADMET chemistry. The likely explanation for this is that steric hindrance prevents the formation of the required metallacycle (3) for productive metathesis between monomer units, as illustrated in the polymerization cycle.

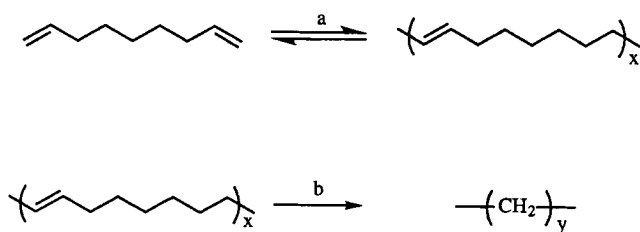
In order to prove this point, one of the methyl groups can be omitted, upon which only dimerization occurs through the 5,6-olefin bond to produce an "unreactive dimer molecule" in quantitative yields. The same experiment can be conducted by placing the methyl groups at the 3,4-position in 1,5-hexadiene, which also prevents ADMET chemistry from occurring. Several other examples of steric effects on polymerization (Konzelman and Wagener, 1995) are also



**Figure 4-9.** Structure reactivity study of nonconjugated hydrocarbon dienes.

illustrated in Fig. 4-9. It quickly becomes evident that steric interactions preclude easy metathesis polymerization unless the substituent is at least beta to the metathesizing double bond. More forceful conditions may permit monomers to bypass this rule, although this has yet to be demonstrated.

The facile nature of hydrocarbon polymerization by ADMET can be exploited to synthesize well-defined macromolecules, and as a consequence it has been possible to synthesize the simplest known hydrocarbon polymer, i.e., polyethylene, with no apparent branching. It is generally accepted that polyethylene prepared by chain polymerization possesses branching of varying degrees of complexity depending upon the type of initiation used in the polymerization. Perfectly linear polyethylene with no observed branching has been prepared by ADMET



a)  $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2)(\text{OCMe}(\text{CF}_3)_2)_2$ , neat,  $\leq 10^{-5}$  mm Hg

b)  $\text{TsNHNH}_2$ ,  $n\text{-Pr}_3\text{N}$ ,  $o\text{-xylene}$ , reflux

**Figure 4-10.** Synthesis of perfectly linear polyethylene via ADMET polymerization of 1,9-decadiene followed by hydrogenation.

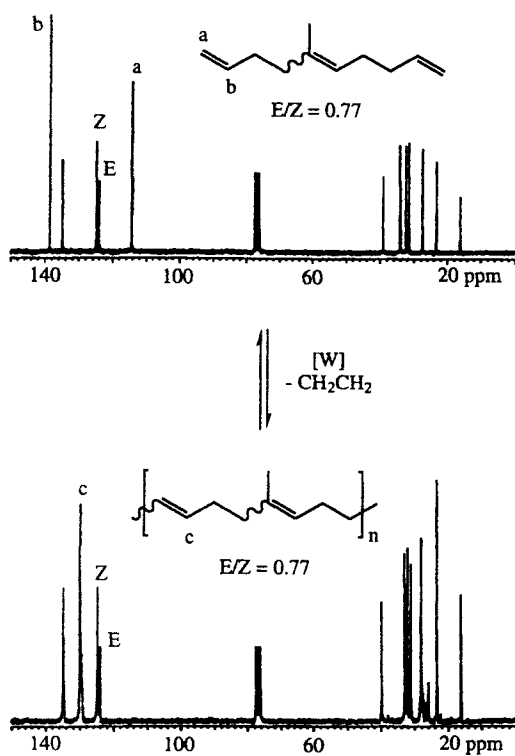
techniques (Fig. 4-10), since only one repeat unit is present in the parent polymer.

For example, 1,9-decadiene can be condensed to polyoctenylene followed by exhaustive hydrogenation with *p*-toluenesulfonylhydrazide (O’Gara et al., 1993 b). Weight average molecular weights in the range of 40 000 can be prepared in this manner, and all experimental evidence collected on these samples supports the conclusion that the polymer is perfectly linear. Hydrogenation advances the crystalline melting point of the unsaturated polymer from about 67°C for polyoctenylene to a very sharp melting point endotherm of 134°C for perfectly linear polyethylene (Mandelkern et al., 1953). Further, the molecular weight after hydrogenation remains essentially the same. These linear polyethylene “model” polymers can provide better understanding of the thermal and mechanical behavior of polyethylene and its copolymers.

Copolymerizations are also possible via ADMET polymerization. Hydrocarbon monomers, such as 1,5-hexadiene and 1,9-decadiene, can be copolymerized to produce random copolymers. Since each of the olefins is of equal reactivity, a statistical distribution of repeat units is expected when using highly active, well-defined catalysts to construct random copolymers. For

example, the tungsten version of Schrock’s alkylidene has been quite effective in producing high molecular weight copolymers in this way. Determination of the random nature of this polymerization has been accomplished by  $^{13}\text{C}$  NMR spectroscopy, where each of the crossover carbons between 1,5-hexadiene and 1,9-decadiene generated repeat units can be resolved unequivocally (Konzelman et al., 1990). These analyses, when compared with the statistically generated data, demonstrate the random placement of comonomers in this copolymerization.

As noted earlier, the activity of an olefin is directly influenced by steric considerations, and thus interesting copolymers can be prepared by exploiting these observations. For example, Fig. 4-11 describes the polymerization of 5-methyl-1,5,9-decatriene. The monomer possesses three olefin bonds, two of which are reactive towards metathesis and one of which is not. The internal olefin is sterically blocked from metathesis and is carried into the repeat unit of the polymer without change. Thus the polymerization produces a perfectly alternating butadiene-isoprene copolymer (Konzelman, 1993). Perfectly alternating copolymers made from a single monomer represent a rare opportunity for the implementa-



**Figure 4-11.** Perfectly alternating copolymer from a single monomer via ADMET polymerization.

tion of ADMET polymerization reactions. Other copolymerizations are possible and remain under study.

#### 4.4.2 Conjugated Dienes

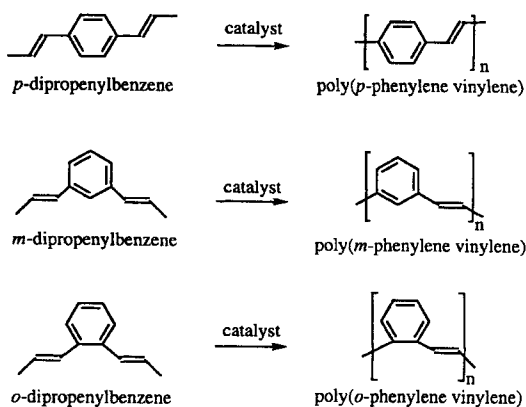
While nonconjugated aliphatic dienes polymerize in a manner that is easily explained, conjugated dienes currently remain somewhat of a mystery in terms of their behavior. The reactivity of both aromatic and aliphatic dienes towards ADMET polymerization has been examined and is described in this section.

Aromatic dienes (Tao, 1994; Wolf and Wagener, 1991) polymerize rather well under ADMET conditions, as illustrated in Fig. 4-12. Therefore it is possible to produce three isomers of poly(phenylenevinylene)

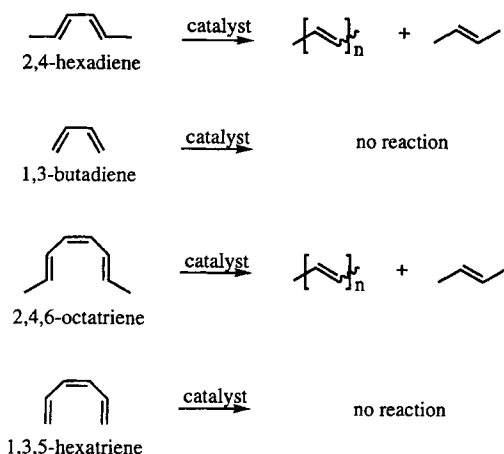
in this manner where the apparent rate of polymerization is determined to a certain extent by the type of isomer used. While *p*-dipropenylbenzene polymerizes rapidly, the *ortho*- and *meta*-derivatives propagate at a slower rate. This can be attributed to intramolecular  $\pi$  complexation between the growing metallized chain end and the penultimate olefin unit in the polymer chain.

The behavior of aliphatic conjugated dienes (Tao and Wagener, 1994) is illustrated in Fig. 4-13. It can be seen that 2,4-hexadiene polymerizes rapidly to yield methyl terminated polyacetylene, as does the analogous monomer 2,4,6-octatriene. Both of these compounds possess terminal methyl groups. However, 1,3-butadiene and 1,3,5-hexatriene do not polymerize at all.

In order to gain insight into this phenomenon, the copolymerization of 2,4-hexadiene and 1,9-decadiene was attempted (Tao, 1994) with both the tungsten and molybdenum versions of Schrock's alkylidene. In both cases, only unreacted monomers and polyoctenamer oligomers were obtained. It is believed that the 1,3-butadiene that is generated during the reaction is poisoning the catalyst, prohibiting copolymer formation. To test this speculation, a mixture of "methyl-terminated" monomers 2,4-hexadiene



**Figure 4-12.** Polymerization of aromatic dienes.



**Figure 4-13.** Study of aliphatic conjugated dienes in ADMET polymerization.

and 2,10-dodecadiene, was exposed to the Schrock catalyst, and poly(acetylene-*co*-octenylene) was formed.

These findings suggest that  $\pi$  complexation between the polymerizing metallized end and a penultimate olefin, either in the monomer or in the growing polymer chain end, poisons the catalyst, thereby preventing polymerization. The effect of the methyl group is apparently to disrupt this  $\pi$  complexation, permitting propagation to occur. This concept is presently speculation, and the area of conjugated dienes continues to be actively investigated.

## 4.5 Functional Groups in ADMET Chemistry

### 4.5.1 The Ether Functional Group

Initially, the thought of conducting metathesis chemistry in the presence of functional groups was considered to be unlikely due to “poisoning” of the active metal center by nonbonded electrons present in the functional group. This Lewis-base phenomenon was demonstrated previously, where

olefins were shown not to metathesize at all (Schrock et al., 1989). In fact, metathesis chemistry can occur in the ADMET reaction only if the olefin group is properly positioned with respect to the functional group in the monomer.

As a first example of this point, Fig. 4-14 shows a structure/reactivity study of ether-containing dienes under ADMET bulk condensation conditions (Brzezinska and Wagener, 1991). Thus divinyl ether and diallyl ether essentially produce no polymer, whereas bis-butenyl ether condenses to release ethylene. Further, as the number of methylene spacers between the oxygen and the olefin increases, the reaction proceeds at a rate sufficient to form polymer. Subtle changes in monomer design induce dramatic changes in reactivity toward ADMET polymerization. These observations lead to two conclusions: first, in spite of prior speculation within the field, intermolecular poisoning of the catalyst system is not sufficiently important to prevent ADMET polymerization occurring, and second, proper spacing of the functional group within the monomer itself prevents intramolecular poisoning from happening. We term this latter observation “the negative neighboring group effect”.

<u>Monomer</u>	<u>ADMET Active?</u>
	NO
	NO
	Sluggish
	YES
	YES

**Figure 4-14.** Effects of the ether functional group on ADMET condensation.

### 4.5.2 Functionality and the Negative Neighboring Group Effect

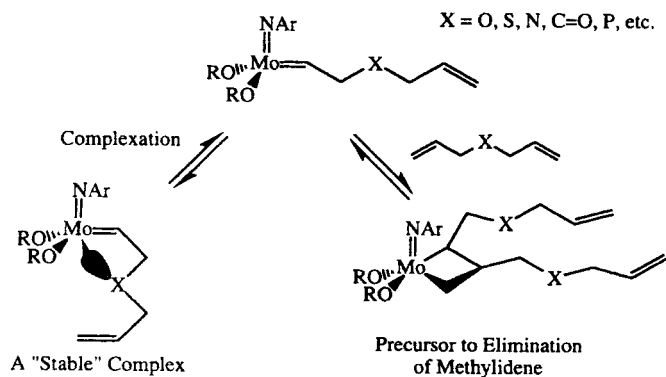
Figure 4-15 illustrates how the negative neighboring group effect operates. For example, if the functional group (X) between dienes possesses Lewis-basic atoms, then intramolecular complexation can occur, shifting the equilibrium to the left and generating a "stable" complex which is metathesis inactive. This intramolecular poisoning is apparently important with spacings of less than two methylene units, for no propagation is apparent in this case. However, as the spacing increases, the equilibrium shifts to the right, leading to the propagation of monomer units as shown in Fig. 4-8. Therefore, if the potentially poisoning functional group is kept at least beta to the metathesizing olefins, the negative neighboring group effect is overruled and productive metathesis occurs.

Systematic investigations of structure/reactivity relationships along with a thorough understanding of the negative neighboring group effect have permitted many functional groups to be included in ADMET polymers, as illustrated in Fig. 4-16. Lewis-base functionalities such as amines (Portmess and Wagener, 1995; Portmess and Wagener, 1996) and thioethers (O'Gara et al., 1993 a) have been shown to follow similar

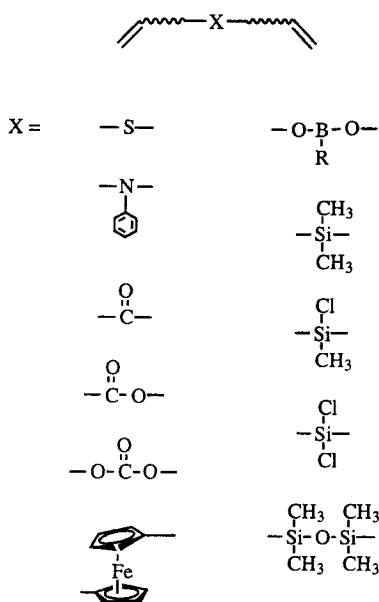
reactivity trends to the analogous ether dienes. These compounds polymerize easily once two methylene units remove the functionality from the olefin.

Carbonyl-containing dienes were originally assumed to be metathesis inactive, since the carbonyl functionality reacts in a Wittig-like manner with the alkylidene to generate a metathesis-inactive metal-oxo species (Schaverien et al., 1986). However, knowledge of the negative neighboring group effect has permitted esters (Patton and Wagener, 1992 b), carbonates (Patton and Wagener, 1992 a), and sterically hindered ketones (Patton et al., 1992) to be polymerized under ADMET conditions. The requirements for the polymerization to be successful are that the carbonyl group must be placed at least beta to the metathesizing olefin, and in the case of ketones the carbonyl must be sterically hindered by geminal methyl groups on the alpha carbons. This steric hindrance serves to block the carbonyl from coordination with the active metal center.

In addition to these Lewis-basic functional groups, a variety of other functional groups can be incorporated into polymers made by ADMET condensation. Electron-deficient boranes and boronates (Wolfe and Wagener, 1996) have been polymerized, and even ferrocenyl units (Boncella et al., 1992)



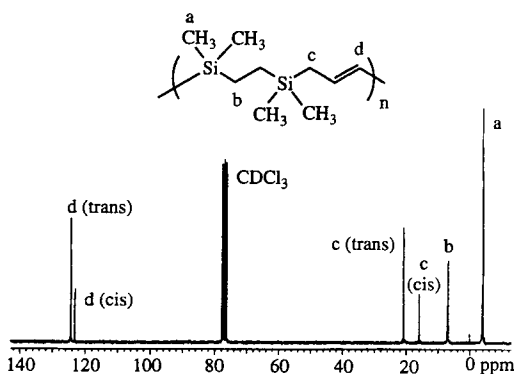
**Figure 4-15.** The negative neighboring group effect.



**Figure 4-16.** Functional groups that have been included in ADMET polymerization.

have been shown to be stable to ADMET polymerization. A broad range of unsaturated silicon-containing polymers has also been studied, including carbosilanes (Wagener and Smith, 1991), carbosiloxanes (Smith and Wagener, 1993), and chlorosilanes (Cummings et al., 1995).

Although the negative neighboring group effect plays no role in the polymerization of organosilane monomers, steric crowding in the proximity of the olefin hinders polymerization. Monomers substituted at the allylic position, such as dimethyldivinylsilane, do not polymerize in the presence of a Schrock alkylidene (Wagener and Smith, 1991). Once these substitutions are removed to at least beta to the olefin, metathesis occurs. Dialkylsilane exhibits no resistance to metathesis polymerization and generates clean polycarbosilanes (Fig. 4-17).

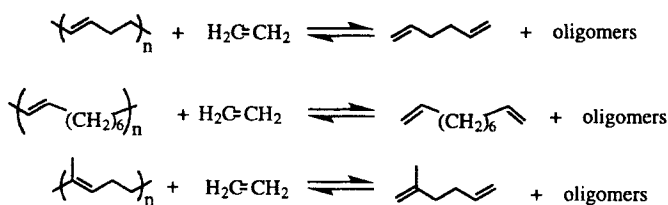


**Figure 4-17.** Synthesis of polycarbosilanes via ADMET polymerization.

## 4.6 ADMET Depolymerization

As mentioned in Sec. 4.3 the ADMET reaction is an example of equilibrium step polymerization chemistry, and as such the reverse reaction can occur when an excess of either ethylene or a 1-alkene is present in the reaction mixture. This process, known as ADMET depolymerization, is quite useful for creating small molecules from rather conventional polymers such as 1,4-polybutadiene, and could be applied to any unsaturated polymer which does not invoke steric or negative neighboring group considerations.

While ADMET polymerization is best done under bulk conditions to maximize the molar concentration of endgroups and to minimize intramolecular cyclization, depolymerization chemistry is accomplished in solution. For example, ethylene can depolymerize 1,4-polybutadiene, poly(octenylene), and even polyisoprene in toluene (Wagener et al., 1991) using Schrock alkylidenes as catalysts (Fig. 4-18). The number average molecular weights of the polymers are decreased from values greater than 100 000 to generate oligomers of 2000 to 5000. The oligomers are very clean, as noted by NMR spectroscopy. Complete depol-



**Figure 4-18.** ADMET depolymerization of 1,4-polybutadiene, polyoctenylene, and polysioprene.

merization with ethylene has not proven possible, however, most likely due to the fact that excess ethylene coordinates with the catalyst, rendering it inactive for metathesis (Robbins et al., 1991). Consequently, the reactions slow dramatically as the active catalyst concentration decreases.

Complete depolymerization is possible, however, if 1-alkenes (e.g., substituted ethylenes) are used in the place of ethylene. Thus, when an unsaturated polymer is combined with an appropriate metathesis catalyst followed by the introduction of an appropriate mono-olefin like ethylene or another 1-alkene, depolymerization ensues to generate mass-exact oligomers of various molecular weights (Marmo and Wagener, 1993). The degree of depolymerization depends upon the ratio of 1-alkene to the number of sites of unsaturation in the macromolecule. Reaction conditions also play an important role in this chemistry.

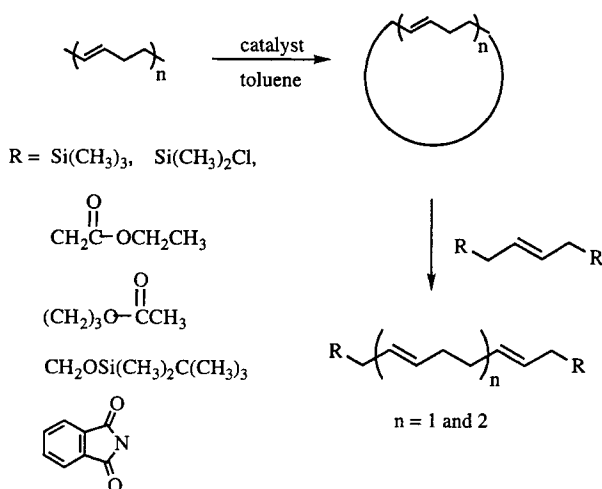
The mechanistic events associated with depolymerization are somewhat different from those associated with ADMET polymerization, principally because the nature of the equilibrium in solution is different from that observed in the bulk. Placing an unsaturated monomer in solution in the presence of a metathesis catalyst leads to the formation of an equilibrium concentration of cyclics, which are generated in high concentration in dilute solution. Thus the first actual "depolymerization" involves the formation of rings. These cyclics then react with the 1-alkene, which is added at a later stage, and, when solvent is removed, mass-

exact oligomers are formed. Examples of such depolymerizations are shown in Fig. 4-19.

When the 1-alkene chosen for depolymerization contains a functional group, perfectly difunctional telechelics can be constructed (Fig. 4-19). For example, 1,4-polybutadiene has been successfully depolymerized under these conditions to yield telechelic oligomers, and even monomers possessing diester, disilyl ether, and diimide functionalities (Marmo and Wagener, 1995). Protected amine, alcohol, and carboxylic acid functionalized (Marmo and Wagener, 1994) telechelics have also been generated in a similar manner. This discovery holds great potential in the area of polymer recycling, since it provides a very clean method for producing small difunctional molecules from large polymers. These telechelics could be further utilized as reagents in organic synthesis or as monomers in condensation polymerizations.

## 4.7 Conclusions

The research completed during the last few years amply demonstrates that acyclic diene metathesis (ADMET) polymerization is useful step polymerization chemistry capable of creating pure hydrocarbon homo- and copolymers, as well as polymers possessing functional groups. The polymerizability of any given monomer is determined both by steric and electronic considerations, and the technique is quite broad in scope.



**Figure 4-19.** Synthesis of telechelic oligomers via ADMET depolymerization of 1,4-polybutadiene.

Further, the depolymerization chemistry that has been accomplished suggests opportunities for the synthesis of difunctional telechelic oligomers, the preparation of fine organics, and for polymer waste recycling.

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## 5 Transition Metal Catalyzed Olefin, Cycloolefin, and Styrene Polymerization

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## List of Symbols and Abbreviations

$k_{11}, k_{12}, k_{21}, k_{22}$	rate constants
$k_p$	polymerization rate constant
$M$	molar mass
$M_n$	number-average molecular weight
$M_w$	weight-average molecular weight
$n$	number
$r_1, r_2$	copolymerization parameters
$r_E$	copolymerization parameter of ethylene
$r_p$	copolymerization parameter of propylene
$R_p$	polymerization rate
$T_g$	glass transition temperature
$T_m$	melting temperature
$x, y$	number
$[\Phi]^{28}_{405}$	molar optical rotation
acac	acetylacetonate(-o)
Benz	benzanellation
Bu	butyl
CDT	cyclododecatriene
COT	cyclooctadiene
Cp	$\eta^5\text{-C}_5\text{H}_5$
E	ethylene
EPDM	ethylene/propylene/diene rubber
EPM	ethylene/propylene rubber
ESR	electron spin resonance
Et	ethyl
HDPE	high density polyethylene
LDPE	low density polyethylene
LLDPE	linear low density polyethylene
Ln	rare earth metal
M	metal
MAO	methylaluminoxane
Me	methyl
Naph	naphthyl
NMR	nuclear magnetic resonance
P	propylene
Ph	phenyl
PP	polypropylene
Pr	propyl
PS	polystyrene
PVC	polyvinylchloride
ROMP	ring opening metathesis polymerization
SHOP	shell higher olefin process
VLDPE	very low density polyethylene

## 5.1 History and Trends

The discovery of transition metal catalyzed olefin polymerization during the early 1950s represents a landmark in the history of sciences and industry with outstanding impact on the development of modern commodity and specialty polymers, as well as modern technologies. The production of more than one third of plastic materials, amounting to approximately 40 million tons per year, involves transition metal catalyzed olefin polymerization. Polyolefins such as polypropylene and polyethylene combine low price with strength, stiffness, impact resistance, low weight, corrosion resistance, versatility in applications, recycling capability, and applications ranging from automotive parts to packaging and textile fibers. Crude oil and polyolefins are hydrocarbons with very similar molecular structures, a similar high energy content, but different molar masses. Therefore, as displayed in Fig. 5-1, polyolefins offer the attractive potential for generating efficient product life cycles: Crude oil is cracked to form olefin monomers, which are polymerized with highly efficient catalysts in solvent-free

processes to form polyolefin materials retaining oil-like high energy contents. When the polymer products lifetime is completed, the polyolefins are converted quantitatively back into liquid and gaseous hydrocarbons upon thermal degradation at temperatures typically above 400 °C. Such hydrocarbon fractions can serve as sources of energy or chemical feedstocks, which substitute oil and natural gas. No other materials can match this extraordinarily attractive energy balance of environmentally friendly polyolefins. It is obvious that catalytic exothermic polymerization with very low energy consumption and no solvent emission is playing a key role.

Polyolefins represent a very young class of materials. Free radical ethylene polymerization, developed by ICI during the mid-1930s, is initiated with radical initiators such as peroxides, and requires high polymerization temperatures (above 150 °C) and very high pressures exceeding 2000 atm (2000 MPa), to produce high molecular mass polyethylene. As a result of chain transfer reactions occurring during free radical polymerization, as shown in Fig. 5-2, high pressure polyethylene contains short and long chain branches, which reduce the polyethylene's crystallinity and consequently also its density. Therefore this class of polyolefins became known as low density polyethylene (LDPE).

In 1953 Karl Ziegler at the Max-Planck Institut für Kohlenforschung in Mülheim an der Ruhr observed that aluminum alkyls insert ethylene into aluminum carbon bonds ("Aufbaureaktion", Fig. 5-3) to form low molecular weight paraffins. This ethylene insertion process is catalyzed by transition metal compounds, e.g., alkoxides and halides of zirconium and titanium, which are activated according to Ziegler by means of aluminum alkyls, e.g., triethylaluminum, thus producing much higher molecular mass

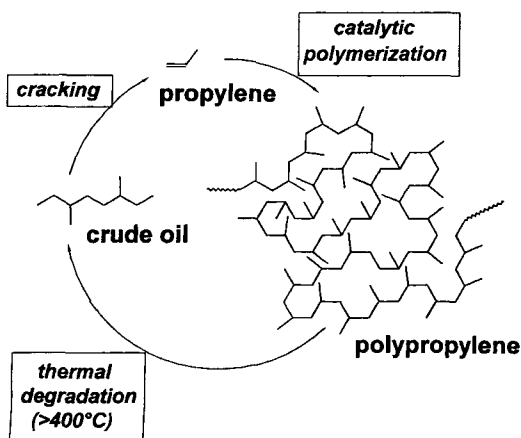
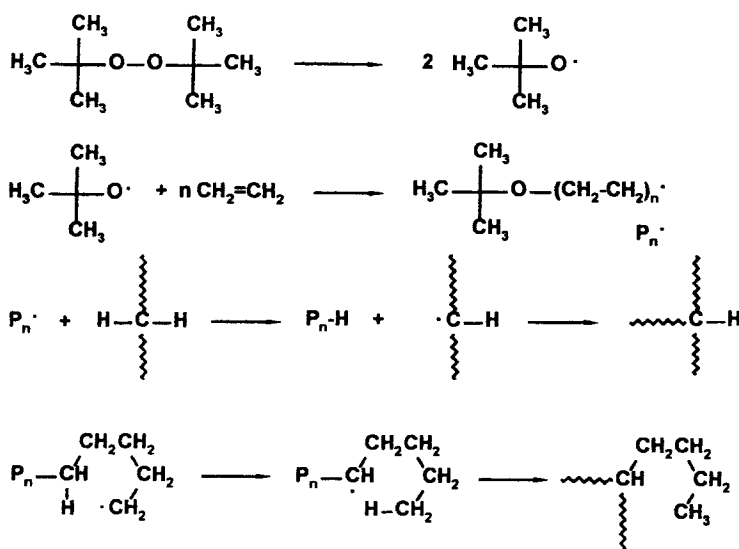
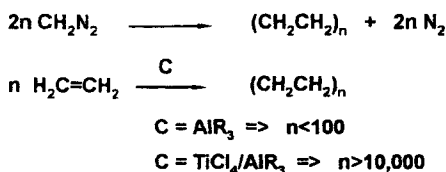


Figure 5-1. The polyolefin life cycle.



**Figure 5-2.** High pressure free radical ethylene polymerization producing low density polyethylene (LDPE).

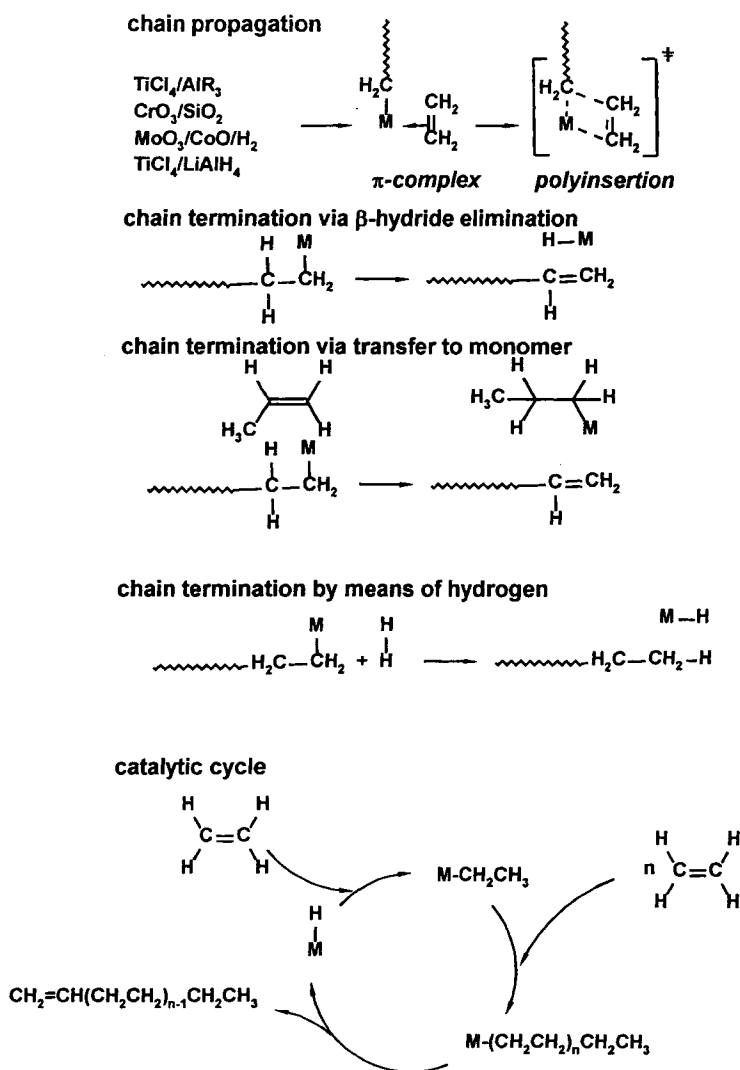
linear polyethylenes. Transition metal catalysts for olefin polymerization, which require activation by means of main group metal alkyls, became known as Ziegler catalysts. In contrast to high pressure free radical processes, catalytic polymerization takes place at room temperature and atmospheric ethylene pressure ("Mülheimer Niederdruckverfahren"). The resulting polyethylene is linear with higher crystallinity and higher density compared to the LDPE reported earlier. Linear polyethylene is also referred to as high density polyethylene (HDPE), which was first prepared at the end of the 19th century on a laboratory scale by thermally decomposing diazomethane (see Fig. 5-3).



**Figure 5-3.** Synthesis of polymethylene by means of diazomethane decomposition and of high density polyethylene (HDPE) by transition metal catalyzed ethylene polymerization. C denotes the catalyst.

Also during the 1950s the Philipps Petroleum Company disclosed activator-free catalyst systems consisting of  $\text{CrO}_3$  on silica gel. Standard Oil of Indiana used  $\text{MoO}_3/\text{CoO}$  mixed metal oxide catalysts which were pretreated with hydrogen. Ziegler and Phillips catalysts, as well as other catalyst systems, function according to the same principle, as displayed in Fig. 5-4. Transition metal alkyls, formed either by alkylation with aluminum alkyls or by reducing chromium(VI) with ethylene, activate ethylene by  $\pi$ -complex formation, thus promoting ethylene insertion into the transition metal alkyl bond. Today, it is well established that chain growth occurs exclusively at the transition metal center. Chain termination results from  $\beta$ -hydride elimination or cleavage of the transition metal alkyls by means of hydrogen, which is used as a chain transfer agent in industrial processes. Both reaction pathways yield transition metal hydrides, which are considered to be the key intermediates of the catalytic cycle.

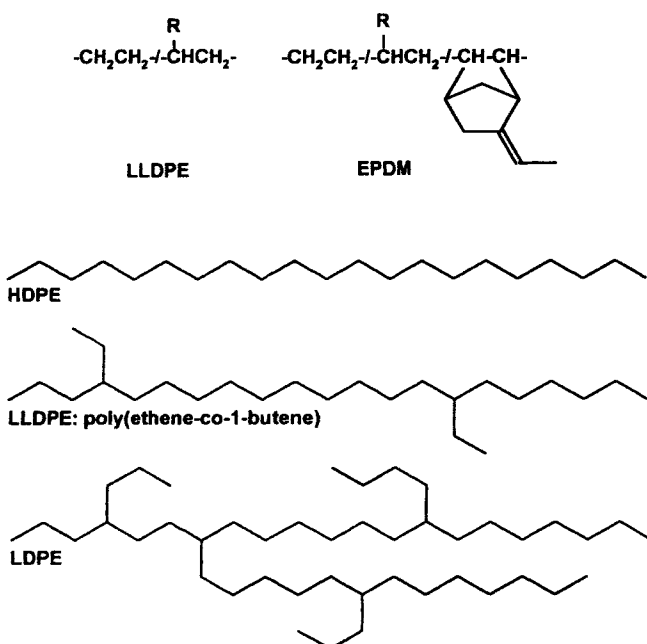
The above-mentioned transition metal catalysts can polymerize ethylene and other nonpolar 1-olefins such as propylene,



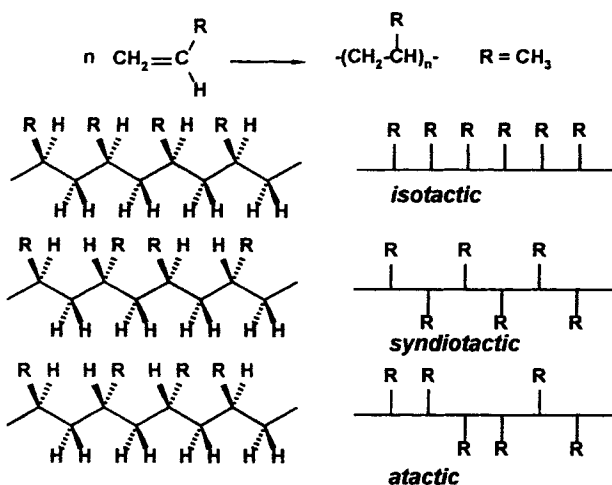
**Figure 5-4.** Elementary reactions and catalytic cycle of transition metal catalyzed ethylene polymerization.

1-butene, 1-hexene, 1-octene, 4-methyl-1-pentene, vinylcyclohexane, dienes, such as butadiene and isoprene, cycloolefins, such as norbornene or ethylidene norbornene, and styrene. Due to steric hindrance, internal double bonds of monomers such as butene-2 and isobutene are frequently not suited for polyinsertion. Most catalyst systems based on group 4 transition metals, such as titanium and zirconium, are severely poisoned by polar monomers, such as carbon monoxide, whereas nickel- and palladium-

based catalysts can tolerate such comonomers (see Sec. 5.5). Copolymerization of ethylene with 1-olefins such as 1-butene, 1-hexene, and 1-octene affords *n*-alkyl side chains which reduce the crystallinity. Such short-chain branched polyethylenes, which are displayed in Fig. 5-5, are referred to as linear low density polyethylenes (LLDPE). An important application is packaging. When 40–70% propylene is copolymerized with ethylene, the resulting poly(ethylene-*co*-propylene)s are completely amorphous



**Figure 5-5.** Ethylene copolymers with 1-olefins to form short chain branched polyethylenes (LLDPE) and rubbers (EPM, EPDM).



**Figure 5-6.** Propylene polymerization and polypropylene stereoisomers.

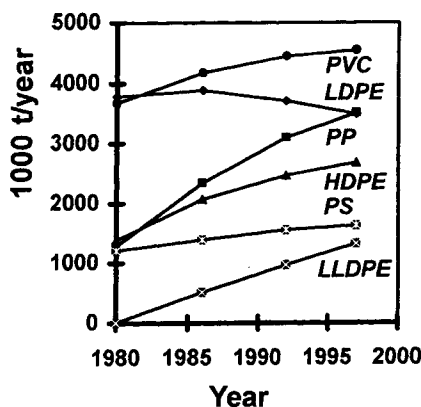
and rubbery. The abbreviation for this saturated hydrocarbon rubber is EPM. Frequently, a few percent of dienes, such as nonconjugated 1,4-hexadiene or ethylidene norbornene, are copolymerized with ethylene/propylene to incorporate olefin side chains, which can be used to crosslink such ethylene/propylene/diene (EPDM, see Fig. 5-5)

polymers by means of sulfur vulcanization.

In 1954, Giulio Natta applied Ziegler's catalyst system to produce isotactic polypropylene. In contrast to ethylene, propylene is prochiral and produces polymers where the repeating unit contains a stereogenic carbon atom (see Fig. 5-6). As a func-

tion of the polypropylene stereochemistry, i.e., the sequence of the two possible configurations of the repeat units, the properties of polypropylene vary over a very wide range. Due to the different solubilities of such diastereoisomers, stereoirregular polypropylenes with a random distribution of the two configurations are soluble in diethylether, whereas highly stereoregular polypropylene is insoluble in boiling *n*-heptane. The stereoirregular polypropylene, which Natta named atactic polypropylene, is amorphous and tacky, with only a few applications, such as hot-melt adhesives. In contrast, the stereoregular polypropylene, where the stereogenic carbon atoms of the repeat units exhibit the same absolute configuration over prolonged sequences of the polypropylene chain, is crystalline and melts at 165 °C. Natta used X-ray diffraction to identify the molecular architecture of isotactic polypropylene. He called this crystalline polypropylene isotactic polypropylene, which is today one of the leading commodity plastics with diversified applications including automotive parts, baby diapers, and membranes. Today, the stereoregularity is readily analyzed by means of  $^{13}\text{C}$ -NMR spectroscopy via the signals of pentad sequences. Spectra of polypropylenes are displayed in Fig. 5-28. The spectrum of isotactic polypropylene exhibits only one methyl group signal typical for the meso (mmmm) pentad, whereas the racemic (rrr) pentad is typical for syndiotactic polypropylene. Stereoselective catalysts were developed to produce stereoregular diene rubbers such as poly(*cis*-1,4-butadiene). The remarkable history of polyolefins is described in reviews by Seymour and Cheng (1989), Pino and Mülhaupt (1980), and Wilke (1995).

The growth of commodity plastics' production in Western Europe is displayed in Fig. 5-7. Innovations in polypropylene cat-



**Figure 5-7.** Western European production of commodity polymers (PVC: polyvinylchloride, PP: polypropylene, LDPE: low density polyethylene, LLDPE: linear low density polyethylene, PS: polystyrene).

alyst and process technology account for the explosive growth of polypropylene production worldwide from less than 1 million tons in the early 1970s to more than 13 million tons during the 1990s. Soon polypropylene production in Western Europe will surpass that of polyvinylchloride (PVC). This is only paralleled by the explosive growth of linear low density polyethylene (LLDPE) in Western Europe from a few hundred tons in 1970 to 1.3 million tons in 1994. As a result of the oil crisis, the quest for energy conservation promoted the production of LLDPE by means of the catalytic low pressure LLDPE processes at the expense of high pressure LDPE production, which is energetically much less favored.

Thirty years ago, nobody expected polypropylene to be so successful. In fact, at that time low catalyst activities and poor stereoselectivities required extensive purification of the obtained polypropylenes. For example, catalyst residues, which cause color formation and corrosion of processing equipment, and low stereoregular tacky polypropylene were removed by means of solvent extraction. Moreover, propylene polymer-



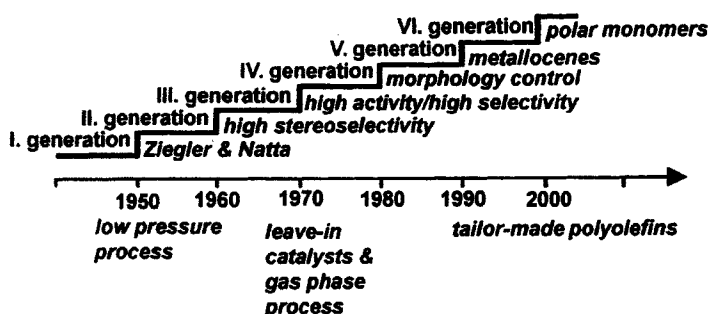


Figure 5-8. Innovations in polypropylene catalyst and process technology.

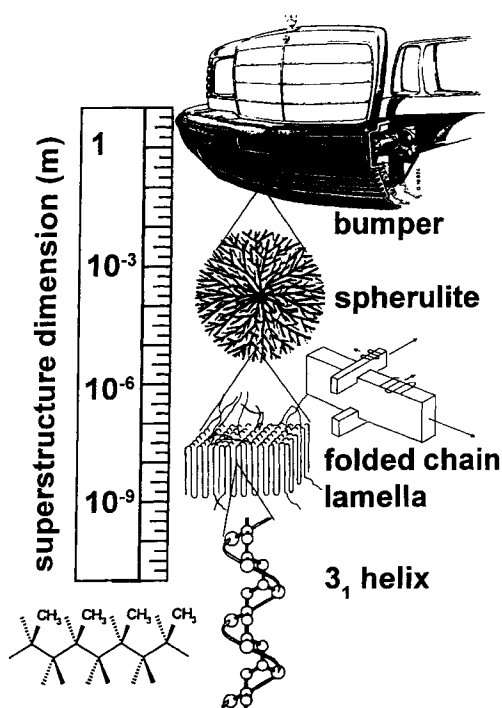
ization using first-generation catalysts was performed as a slurry in nonpolar diluents such as hexane, which required special solvent recovery. For the production of 1 ton of isotactic polypropylene up to 200 kg of waste needed to be disposed of, at that time preferably by landfill. The progress of polypropylene manufacturing and application is reviewed in the polypropylene handbooks published by Moore (1996) and van der Ven (1990). Polypropylene applications include injection-molded parts, films, fibers, and blow-molded containers. The special recycling potential of polypropylene and polyolefins with respect to other plastics is outlined by Brandrup et al. (1996). Polypropylene wastes can be remolded or degraded to recover oil feedstocks as raw material, as schematically presented in Fig. 5-1.

Since the 1950s, polypropylene production has been revolutionized every 15 years. Innovations, as summarized in Fig. 5-8, have promoted the competitiveness of polypropylene, which is today competing very successfully with other materials and other, more expensive and less environmentally friendly polymers. During the 1970s, highly active and stereoselective catalyst generations gave isotactic polypropylene in very high yields without by-product formation. At catalyst activities exceeding 1 ton per gram of titanium (corresponding to 1 ppm residual titanium in the polymer), catalyst residues were left in the polymer (“leave-

in” catalysts). Supported catalysts were the key to gas phase and liquid pool polypropylene processes where the use of solvent was eliminated. As will be reported in Sec. 5.2 in more detail, modern particle-forming catalysts produce pellet-sized polypropylene during polymerization in liquid propylene, thus eliminating the need for pelletizing extrusion. The assignment of numbers for the different generations is somewhat arbitrary because of the extraordinary variety of innovative approaches.

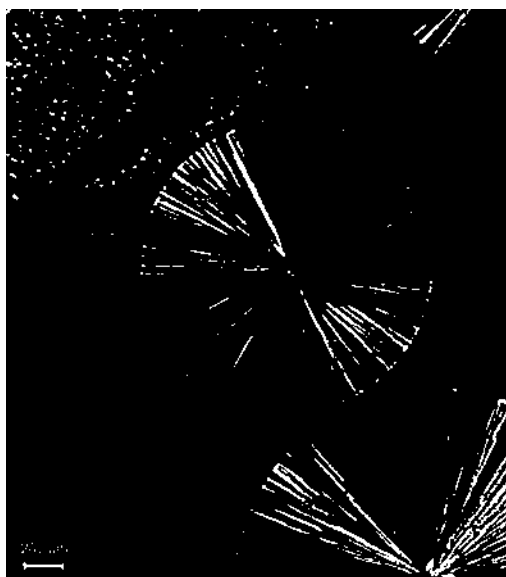
Since the 1980s, novel metallocene catalysts have become available to produce tailor-made homopolymers as well as copolymers of ethylene, propylene, and other 1-olefins, cycloolefins, and styrenes. The advantages of metallocene catalysts are:

- high catalyst activity (“leave-in” catalysts),
- the production of polyolefins with narrow molar mass distribution due to the exclusive presence of a single type of catalytically active site,
- independent control of molar mass, stereoregularity, end groups, long and short chain branching, and comonomer incorporation, and
- the production of very uniform copolymers over the entire comonomer composition range, including comonomers such as long chain 1-olefins, cycloolefins, and styrene.



**Figure 5-9.** Molecular and supramolecular architectures of polypropylene.

Novel catalyst generations, e.g., nickel- and palladium-based catalysts, produce copolymers of nonpolar ethylene and 1-olefins with polar monomers such as carbon monoxide and methyl acrylate (see Sec. 5.5). Similar to the biosynthesis of proteins, which are derived from twenty amino acids, industrial catalysis today converts a small number of petrochemical monomers into a large variety of polymeric materials, with applications ranging from automotive parts, films and thin wall containers for packaging, rubbers, textile fibers, and electrical insulation of appliances to microporous membranes for separation technology. The control of the molecular architecture by tailor-made catalysts is the key to tailor-made polyolefins. As shown in Fig. 5-9, steric control in propylene poly-



**Figure 5-10.** Spherulite formulation by the crystallization of polypropylene from a polypropylene melt, imaged in polarized light and color-enhanced by computer.

merization leads to isotactic polypropylene with a helical conformation ( $3_1$  helix). In the solid state, such helical chains fold to produce crystallites which grow to form spherulites, which are visible in polarized light as Maltesian cross-like structures (see Fig. 5-10). Depending on the polymer configuration and in particular the regio- and stereoregularities, it is possible to control polymer crystallization and to influence the mechanical as well as the optical properties of the resulting polymers. After forty years of mainly trial-and-error-like catalyst development, novel uniform catalysts give a much better insight into the basic correlations between the catalyst and the polymer architectures, as well as the solid state properties. Some of these key principles of catalyst and polymer design are presented in this overview.

## 5.2 Polymerization Processes

The basic scheme of an olefin polymerization process is displayed in Fig. 5-11. Polymerization is initiated by injecting the catalyst, e.g., aluminum alkyl activated transition metal compounds, into the reactor together with the olefin, optional comonomers, diluents, and hydrogen, which controls the molecular mass. The preferred polymerization processes for ethylene polymerization are gas phase, solution, and slurry polymerization (James, 1986). Propylene is polymerized in gas phase and slurry processes (Lieberman and Barbe, 1985). In a slurry process, hydrocarbon diluents, such as hexane or liquid propylene in the case of polypropylene manufacturing, are used. Because such diluents are nonsolvents for the polyolefin, the growing polyolefin precipitates as soon as the chain reaches a critical molecular mass, thus forming particles. Particle morphology is controlled by means of tailored supported catalysts (see Sec. 5.3).

For stable operation it is important to prevent the formation of very small dustlike particles with low bulk densities and to remove the heat of polymerization, which amounts to 108 kJ per 42 g polypropylene! Gas phase polymerization can be performed in stirred tank reactors (see Fig. 5-12) or fluidized bed reactors. The heat of polymerization is removed by cooling the monomer stream. The polymer obtained in gas phase polymerization is recovered in a disengagement zone by vaporizing off and recycling the olefin gas.

In slurry polymerizations, which are performed in stirred tank or loop reactors, the polymer is separated via centrifugation, followed by steaming with water vapor to distill off residual monomer and diluents. Typical reaction conditions for gas phase and slurry polymerizations are temperatures below the melting temperature of polyethylene ( $T_m = 135^\circ\text{C}$ ), usually in the range of  $60\text{--}80^\circ\text{C}$ , pressures of 10 atm ( $1\text{ Mn m}^{-2}$ ), and average hold-up times of 4–8 h. In con-

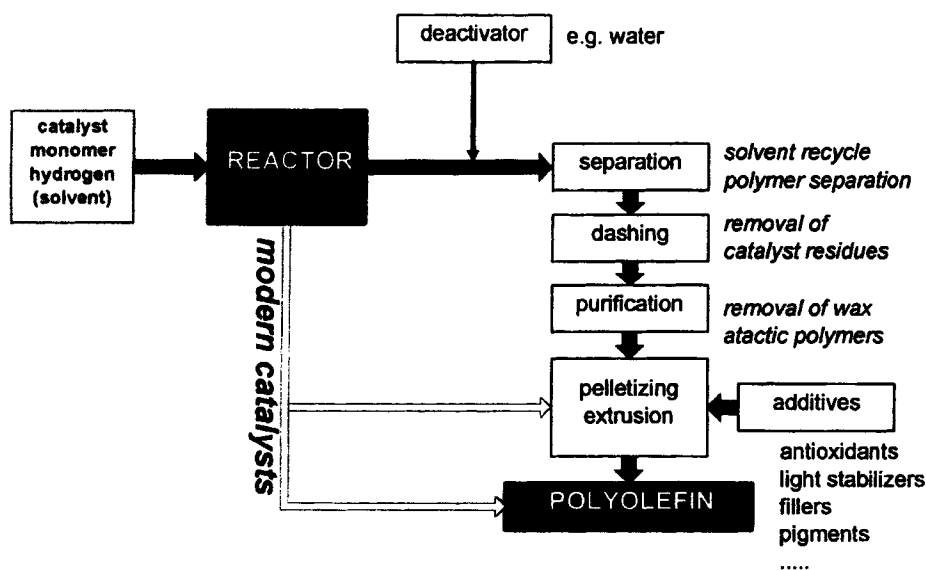
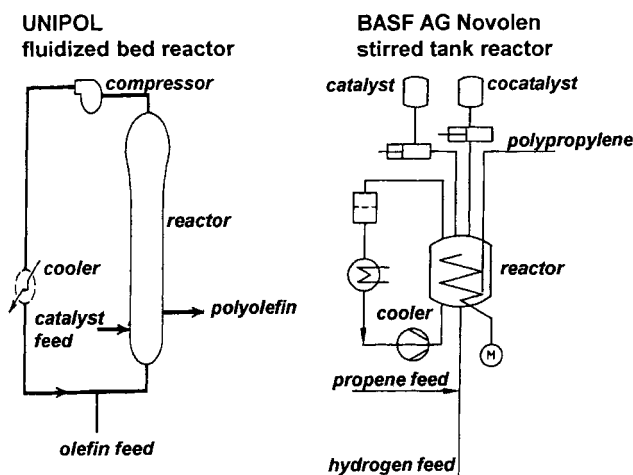


Figure 5-11. Olefin polymerization process.

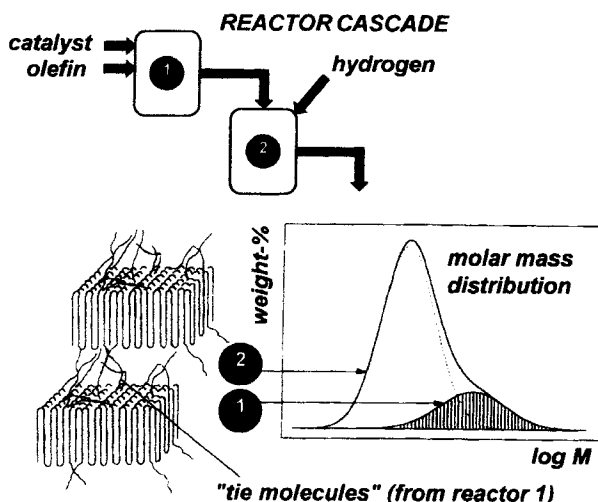


**Figure 5-12.** Gas phase polymerization in a fluidized bed reactor (Unipol process, Union Carbide) and in a stirred tank reactor (Novolen, Targor).

trast, in a solution process, polyethylene is obtained in a solution, e.g., in cyclohexane, at temperatures above the melting temperature of polyethylene, typically in the range of 150–280 °C. Upon cooling below 150 °C, the polyethylene melt phase separates from the cyclohexane and can be extruded. During extrusion, residual solvent is vaporized by applying a vacuum. Due to the very limited lifetime of catalysts at high temperatures, such polyethylene solution processes operate at much shorter hold-up times of 10–30 min and higher pressures of approximately 100 atm (100 MPa). At higher temperatures, the degree of efficiency of energy recovery is enhanced. In fact, the polymerization reaction generates heat which can be used to generate steam. Most commercial polymers are sold as pellets, which are obtained by pelletizing extrusion. During extrusion, stabilizers, e.g., phenolic antioxidants and hindered amine light stabilizers, are added to the polymers. As mentioned earlier, modern catalyst generations are the basis for simplified olefin polymerization processes. Highly active and selective catalysts eliminate both deactivation, e.g., by injecting water or alcohols, and extensive purification, by means of solvent ex-

traction, which was required to remove wax-like low molar mass byproducts, atactic polypropylene, and catalyst residues. With particle-forming supported catalysts (see Sec. 5.3 and 5.4), pelletizing extrusion is also eliminated, because pellet-sized particles are formed in the reactor (Lieberman and LeNoir, 1996). Modern solvent-free processes for producing polyolefins represent environmentally friendly processes with very high efficiencies with respect to the utilization of feedstocks and energy.

Modern polyolefins are tailored in reactor cascades containing two or more reactors in sequence. For example polyolefins with bimodal molar mass distributions are prepared in a two-reactor system, as displayed in Fig. 5-13. In the first reactor, a small amount of very high molecular mass copolymer (molar mass  $>10^6$  g/mol) is produced by catalytic copolymerization in the absence of hydrogen. Then, in the second reactor, hydrogen is added to produce polyethylene with a much lower molecular mass of 100 000–500 000 g/mol. The small fraction of high molecular weight comonomer functions are “tie” molecules between the crystallites, thus enhancing the environmental stress-crack resistance. The produc-



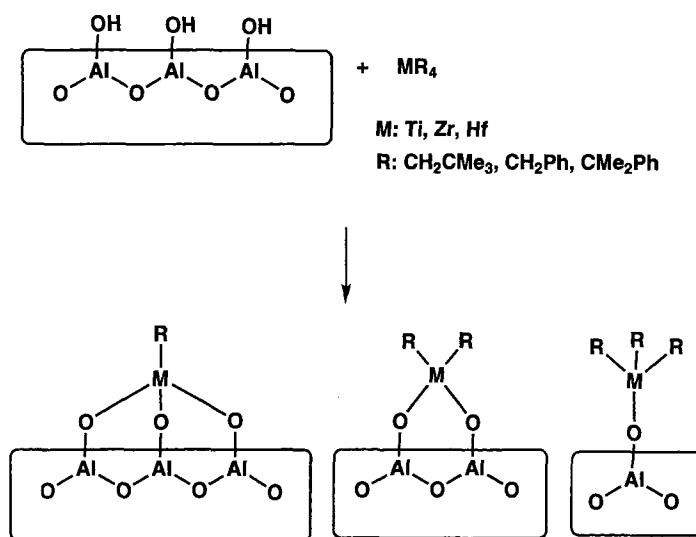
**Figure 5-13.** Polyethylene with a bimodal molar mass distribution, prepared in a reactor cascade.

tion of bimodal polyethylene pipe resins was reviewed by Böhm et al. from Hoechst AG (1992, 1995). As mentioned in Sec. 5.3 in more detail, reactor granule technology, as developed by Montell, employs a sequence consisting of a liquid pool loop reactor combined with a gas phase reactor in order to produce multiphase polymers where either ethylene/propylene rubber is dispersed in polypropylene (Montell's Catalloy technology) or styrene or acrylic monomers are incorporated into micropores of polypropylene by means of free radical polymerization in polypropylene particles (Montell's Hivalloy technology). Reactor cascades continue to play an important role in the tailor-making of polyolefin materials, especially reactor blends, with new property combinations (Galli et al., 1995).

### 5.3 Supported Catalysts and Morphology Control

Both slurry and gas phase processes require tailor-made supported catalysts to achieve stable operation, i.e., constant high

catalyst activity, high stereoselectivity with respect to the formation of isotactic polyolefins, and high bulk density of the resulting polyolefins containing no dust-like polyolefin particle fraction (average particle sizes  $<10\ \mu\text{m}$ ). Even during the pioneering days of transition metal catalyzed olefin polymerization in the 1960s, it was well recognized that catalyst activity is proportional to the number of active centers and monomer concentration (Eq. 5-1). Active center determination revealed that the first generation of Ziegler catalysts gave less than 1% active titanium in propylene polymerization! Since only transition metal alkyls located on the catalyst surface offer free vacant coordination sites for olefin complexation and insertion into the transition metal alkyl bond, catalyst development was directed towards immobilization of transition metal alkyls at the surface of inert support materials with a high specific surface area or a large pore volume. Moreover, during polymerization most first-generation catalysts are embedded in a shell of polyolefins impermeable to the gas which causes severe limitation to monomer diffusion to the active centers. Therefore supported catalysts



**Figure 5-14.** Supported activator-free transition metal alkyls.

are preferred where the catalyst particles undergo fragmentation during polymerization. For activator-free transition metal alkyls, Ziegler–Natta, and metallocene catalysts, different strategies have been employed to produce industrial supported catalysts. It should be noted that there are no universal supports, because the support materials must offer very specific coordination sites which are different for individual transition metal compounds.

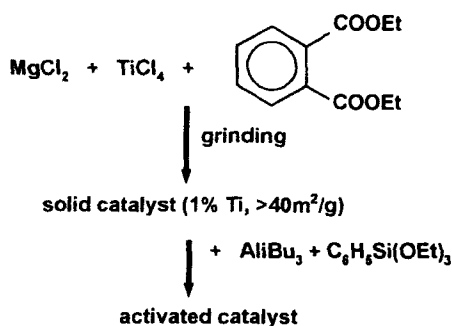
$$R_p = k_p [C^*] [M] \quad (5-1)$$

where  $R_p$  is the polymerization rate,  $[C^*]$  is the active center concentration, and  $[M]$  is the monomer concentration.

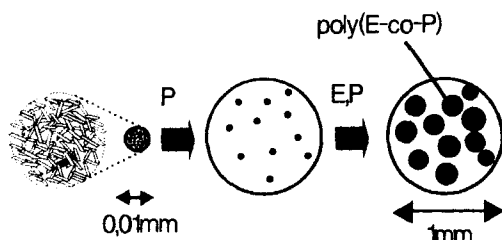
The performance of Phillips-type  $\text{SiO}_2/\text{CrO}_3$  catalysts was improved significantly when low valency chromium was supported on silica. Chromium is attached to the silica support via reaction with silanol groups at the silica surface. Similarly, ICI and Du Pont developed  $\text{Al}_2\text{O}_3$ -supported  $\text{TiR}_4$  and  $\text{ZrR}_4$  ( $\text{R} = \text{CH}_2\text{Ph}$ ,  $\text{CH}_2\text{CMe}_3$ , or  $\text{CH}_2\text{CMe}_2\text{Ph}$ ), where Zr–O bonds were formed between the support surface and the catalytically active transition metal alkyls

(Colette et al., 1989). This reaction pathway is schematically presented in Fig. 5-14.

Another important quest was the development of stereoselective catalysts for the production of isotactic polypropylene using Ziegler–Natta catalysts based upon aluminum alkyl activated titanium halides. Originally, it was believed that only heterogeneous catalysts were able to produce isotactic polypropylene. Therefore extensive research during the last forty years was aimed at the systematic modification of titanium trichloride crystal structures (Boor, 1979). A breakthrough occurred during the late 1960s when  $\text{MgCl}_2$  was applied as a high surface area support in conjunction with Lewis bases as catalyst modifiers. Since the crystal structure of  $\text{MgCl}_2$  is equivalent to that of  $\gamma\text{-TiCl}_3$ ,  $\text{MgCl}_2$  can substitute inactive bulk titanium halides and offers the adequate coordination site at the  $\text{MgCl}_2$  surface. Magnesium halides with high surface areas are produced by different routes, e.g., grinding magnesium salts together with titanium compounds in a ball mill, the chlorination of soluble magnesium alkyls, or the mixing of magnesium alkyls with aluminum



**Figure 5-15.** Preparation of stereoselective  $\text{MgCl}_2$ -supported titanium catalysts.



**Figure 5-16.** Reactor granule technology for polypropylene (Spheripol, Catalloy, and Hivalloy technologies from Montell).

alkyls prior to contact with titanium compounds. This remarkable development was reviewed by Tait and Watkins (1989), Albizzati et al. (1995, 1996), and Chadwick (1995).

According to Fig. 5-15, anhydrous magnesium chloride is ground together with  $\text{TiCl}_4$  and diethyl phthalate as an internal donor to produce high surface area  $\text{MgCl}_2$ -supported catalysts containing 1% Ti. These catalysts are composed of agglomerates of very small primary catalyst particles. The addition of internal donors prevents irreversible agglomeration of such nanoparticles and promotes deagglomeration during polymerization. The solid catalyst is activated with aluminum alkyl containing an external donor, preferably a silane or diether. At aluminum/donor molar ratios  $>1$ , the external

donor can selectively poison nonstereoselective, catalytically active sites. Such less stereoselective sites are complexed (preferably), because low stereoregularity is due to less steric hindrance, which causes higher Lewis acidity with respect to the highly stereoselective, less Lewis acidic sites. Today the use of 1,3-diethers has eliminated the need for external donor addition.

During the 1980s Galli and co-workers at Montedison – now Montell – discovered that the solid catalyst acts as a template for the formation of the polypropylene particles. Spherical catalyst particles, form spherical, pellet-sized polypropylene particles. In Montell's Spheripol process such particle-forming catalysts eliminate the need for pelletizing extrusion, thus simplifying olefin polymerization processes (Albizatti et al., 1996). During the 1990s, advanced morphology control catalyst systems were developed for use in Montell's reactor granule technology (Galli, 1995) (Fig. 5-16). Depending on the catalyst morphology, it is possible to control the porosity of the polypropylene particles. Microporous polypropylene granules have been used to incorporate separate microphases into the continuous polypropylene matrix. In Montell's Catalloy technology, ethylene/propylene copolymerization is performed in the gas phase using the polypropylene granules (formed in liquid propylene) as "micro-reactors". Since the deagglomeration process accounts for the uniform distribution of catalytically active sites throughout the particles, EPM rubber microphases are incorporated in the second gas phase reactor by copolymerizing ethylene with propylene inside the polypropylene spheres. Moreover, microporous granules are used in Montell's Hivalloy process to incorporate microphases of polystyrene or acrylic polymers, which are polymerized in such polypropylene micropores by a free radical

mechanism. Morphology control is the key to polypropylene reactor blends for applications such as engineering plastics, which exhibit improved properties such as a combination of stiffness, strength, impact resistance, and higher heat distortion temperature.

Special supported catalysts have been developed for metallocene-catalyzed gas phase polymerization. In order to preserve the single site nature of the homogeneous metallocene catalysts, they are adsorbed in porous silica which is first dehydrated and coated with methylalumoxanes. The prospect of metallocene-catalyzed gas phase polymerization was reviewed by Hungenberg et al. (1995).

## 5.4 Polymerization Mechanisms and Stereoselectivity

### 5.4.1 History and Principles of Metallocene Catalysis

Soon after the epoch-making discovery of Ziegler–Natta catalysts, metallocene complexes were used as soluble models for heterogeneous systems, the predominant catalysts for commercial use in polyolefin production. The combination of alkyl aluminum compounds and titanocene complexes such as  $\text{Cp}_2\text{TiCl}_2$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) was found to be moderately active for the polymerization of ethylene but failed to polymerize  $\alpha$ -olefins (Natta et al., 1957; Breslow and Newburg, 1957). The Cossee–Arlman model for the polyinsertion mechanism, published in 1964 (Arlman and Cossee, 1964), had to remain without direct proof from the coordination chemistry point of view. In the 1970s several groups noticed the activating effect of traces of water, commonly believed to be a strong catalyst poison, in such metallocene systems. Thus the addition of a small amount of water ( $\text{Al}:\text{H}_2\text{O} =$

1:0.05–0.3) improved the productivity of the catalyst system  $\text{Cp}_2\text{TiEtCl}/\text{EtAlCl}_2$  significantly, and this finding was attributed to the formation of aluminoxanes resulting from the partial hydrolysis of aluminum alkyls (Sinn and Kaminsky, 1980). After the preparation of methylaluminoxane (MAO) as a most efficient cocatalyst for metallocene complexes of group 4 metals in the late 1970s, the stage was set to develop structurally well-defined polymerization catalysts on the basis of group 4 metallocenes and to investigate the nature of the active species in Ziegler–Natta catalysis on the molecular level. Even more intriguing is the fundamental possibility of controlling the tacticity of polypropylene through the molecular structure of the metallocene catalyst, which was recognized by Ewen (1984) as well as Kaminsky et al. in 1985. Since the pioneering work by Turner and Schrock (1983), Jordan (1991), and others at a later date, it has now been established in a great number of studies that cationic 14-electron alkyl ( $\text{Cp}_2\text{MR}$ )<sup>+</sup> is the active site for chain propagation. Elegant kinetic studies recently performed by the groups of Brintzinger and Bercaw have proved the decisive role of  $\alpha$ -agostic interaction of the growing chain with the transition metal center (Coates and Grubbs, 1996). More recently, worldwide effort has been concentrating on finding a transparent relationship between the ligand properties of the catalyst and the polymer structure, as well as developing novel non-metallocene catalyst precursors for the controlled polymerization of  $\alpha$ -olefins and copolymerizations (Okuda, 1993; Mülhaupt and Rieger, 1996).

From the early days of Ziegler–Natta catalysis on, it was recognized that the metal centers capable of performing polyinsertion of olefins had to have two cis-configured coordination sites (Arlman and Cossee, 1964). One of them would be an “empty”



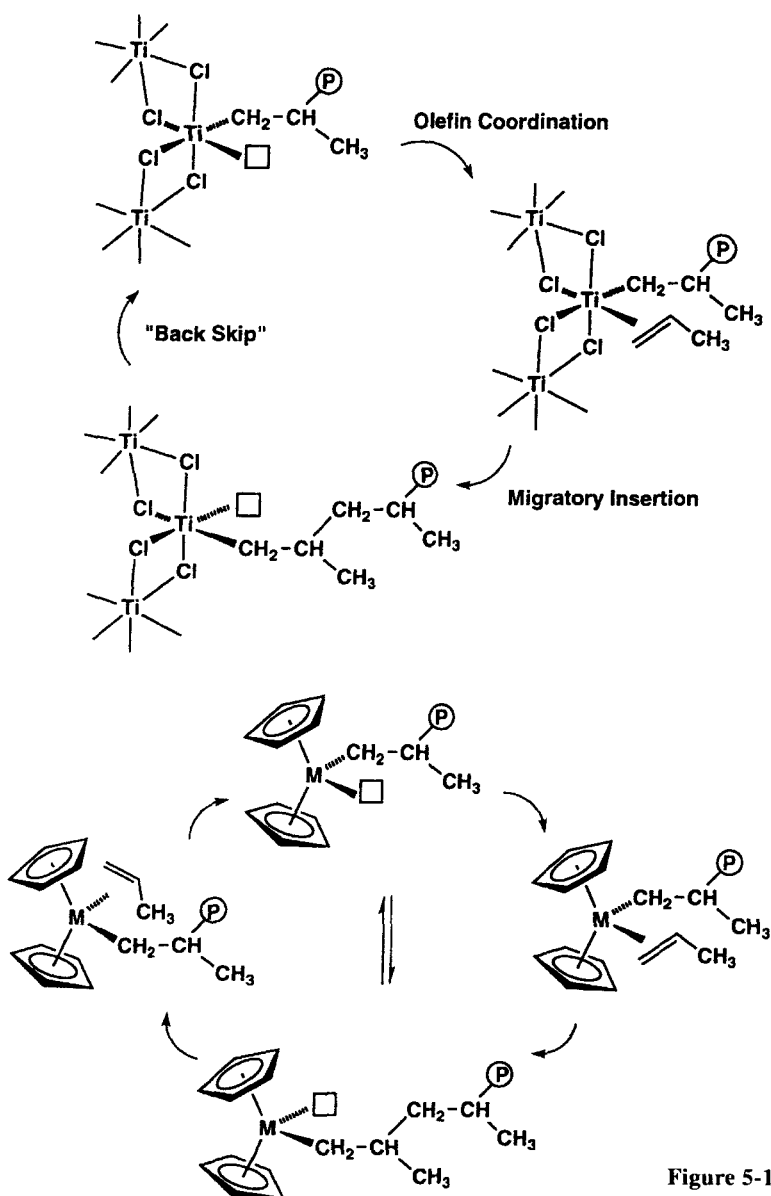


Figure 5-17. Cossee-Arlman mechanism.

site where the olefin monomer would be coordinated and, in the case of the  $\alpha$ -olefin, oriented in a stereospecific way. The other site would carry an alkyl or hydrido ligand into which the olefin inserts, forming a new metal-alkyl bond. Apart from the finer details, the elementary steps occurring on heterogeneous catalyst surfaces and in soluble metallocene complexes should be basically

the same. Thus the chain-growing step can be regarded as a repetitive migratory insertion into the alkyl or hydrido bond, preceded by coordination of the monomer both in the heterogeneous and homogeneous catalysts (Fig. 5-4 and Fig. 5-17).

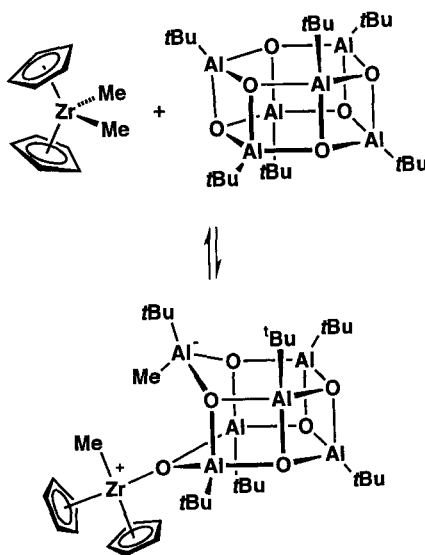
Although the use of methylaluminoxane as the cocatalyst results in a dramatic increase, by several orders of magnitude, of

the efficiency of metallocene catalysts and allows the formation of high molecular weight polyolefins, there is still no completely clear picture of its structure and function. The reaction of trimethylaluminum with water gives a very complex reaction mixture of several aluminum species which still contain sizable amounts of unreacted trimethylaluminum. Based on many different spectroscopic and model studies, it has been established that methylaluminoxane consists of a dynamic mixture of interconverting cage-type oligomers formed from  $\text{AlMe}_2\text{O}$  and  $\text{Me}_2\text{AlOAlMeOAlMe}_2$  units. Both tri- and tetra-coordinate aluminum centers seem to be present. The activating effect of methylaluminoxane can be divided into at least two functions: Firstly, methylaluminoxane and/or the trimethylaluminum contained in the cocatalyst mixture perform alkylation of the metallocene dichloride  $\text{Cp}_2\text{MCl}_2$ , commonly employed as the metallocene component in homogeneous polymerization catalysts to give  $\text{Cp}_2\text{MRCl}$  or  $\text{Cp}_2\text{MR}_2$ . In the case of titanium complexes, it is known that such alkyl species may decompose in a variety of ways, inter alia producing titanium(III) or alkylidene species such as Tebbe's reagent,  $\text{Cp}_2\text{Ti}(\mu\text{-Cl})(\mu\text{-CH}_2)_2\text{AlMe}_2$ . This fact is related to the shorter lifetime of many titanium-based metallocene catalysts.

The second, more crucial function of methylaluminoxane is to generate and stabilize cationic metallocene species by abstracting one anionic (alkyl or chloro) ligand. The Lewis acidic aluminum center is transformed into a tetra-coordinate aluminum center  $\text{AlX}_4^-$ , which as part of a larger cage is capable of distributing the negative charge and functions as a so-called weakly coordinating anion. The existence of cationic metallocenium ions such as  $(\text{Cp}_2\text{ZrMe})^+$  in the presence of methylaluminoxane was confirmed by  $^{13}\text{C}$  and  $^{91}\text{Zr}$  NMR spectroscopy

(Shishta et al., 1992). Using *tert*-butylaluminoxane this elementary step during the activation of metallocene complexes could be simulated (Fig. 5-18).

If the neutral metallocene is regarded as a dormant species, then according to Fig. 5-18 the increase in the number of cationic species is related to the amount of methylaluminoxane employed. In practice, a large excess of methylaluminoxane is required with respect to the transition metal. Molar aluminum:metal ratios of  $>100$  are required, although preferably ratios in the range of 1000 and 5000 mol/mol are employed. Analogous to the earlier metallocene catalysts activated with conventional alkyl aluminum compounds for ethylene polymerization, the elementary steps involve intermittent growth of the polymer chain. During chain growth a very rapid equilibrium is established between the neutral contact ion pair, the dormant species, and the catalytically active cationic species at the chain end. This equilibrium between dormant and active sites is very fast com-



**Figure 5-18.** Model for the function of methylaluminoxane.

pared to chain growth, and does not broaden the molecular weight distribution. In fact, one of the key features of metallocene catalysts is the presence of essentially one type of active center, which produces polyolefins with narrow polydispersity around the theoretically expected value for  $M_w/M_n$  of 2.0 ("single-site catalysts" as opposed to the conventional multi-site catalysts with  $M_w/M_n > 5$ ).

A wide variety of MAO-free cationic metallocene systems has been developed (Jordan, 1991) where the active site for chain propagation, the cationic 14-electron alkyl  $(Cp_2MR)^+$ , is stabilized by a weakly coordinating anion. The simplest way to generate an active system consists of reacting a dialkyl, such as  $Cp_2ZrMe_2$ , with the strong Lewis acid tris(pentafluorophenyl)borane to give  $(Cp_2ZrMe)^+ [MeB(C_6F_5)_3]^-$ . The anionic species (MAO-X) $^-$  can be replaced by other suitable anions

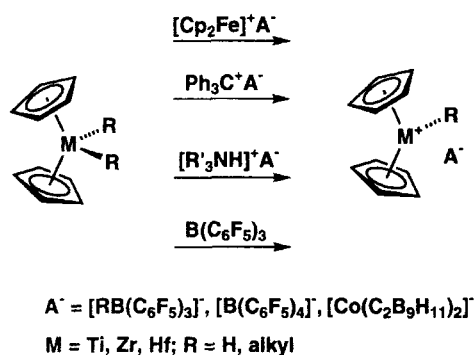


Figure 5-19. Methods of metallocenium formation.

such as perfluorinated tetraphenylborate  $[B(C_6F_5)_4]^-$  or carborane ions  $[M(C_2B_9H_{11})_2]^-$  ( $M = Fe, Co, Ni$ ). Several routes towards generating a cationic metallocene alkyl complex in the presence of a weakly coordinating anion are now possible, and are summarized in Fig. 5-19.

According to crystallographic studies, e.g. of  $(Cp_2ZrMe)^+[MeB(C_6F_5)_3]^-$ , the methyl group bridges zirconium and boron, indicating the presence of a coordinating site at the electrophilic metal for the olefin coordination (Fig. 5-20). Model compounds for the so-called  $\pi$ -complex of olefins have recently been synthesized and demonstrate the exceedingly weak bonding between the  $d^0$  metal center and the olefin (Wu et al., 1995).

Isoelectronic species to the metallocenium ions of group 4 metals are neutral lanthanocene complexes of the general type  $Cp_2LnR$  ( $Ln$  = rare earth metals;  $R = H, alkyl$ ). They can be regarded as single-component catalysts, since they do not require any co-catalysts. Although many systems are highly active (and virtually living, vide infra) in ethylene polymerization, they suffer from low activity towards  $\alpha$ -olefins (Watson and Parshall, 1985). Nevertheless, they offer numerous versatile model systems for the investigation of homogeneous olefin polymerization catalysts.

As a way to control the molecular weight and the molecular weight distribution, as well as to prepare rational block copoly-

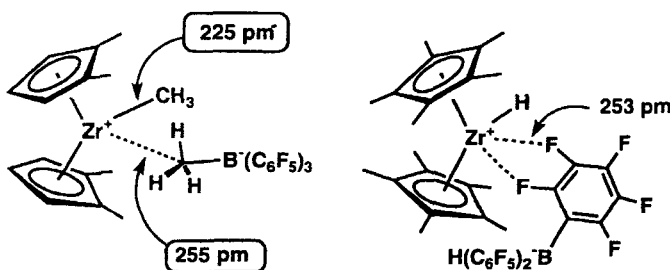


Figure 5-20. Crystallographic structures of metallocenium ions.

mers for the construction of various macromolecular architectures, living or controlled polymerization of olefins has long been a challenge in polymer synthesis. The replacement of multi-site heterogeneous catalysts by structurally defined homogeneous systems has opened up an unprecedented possibility to achieve this goal. An early example of the controlled polymerization of ethylene is performed by a tantalum alkyl complex  $\text{Ta}(\text{PMe}_3)_2\text{I}_2(\text{CH}_2\text{-}t\text{-Bu})$  that tautomerizes to the alkylidene hydrido complex  $\text{Ta}(\text{PMe}_3)_2\text{I}_2\text{H}(\text{=CH-}t\text{-Bu})$  (Turner and Schrock, 1983). Several structurally well-defined complexes were reported to give polyethylene with narrow molecular distributions ( $M_w/M_n < 1.1$ ), suggesting that the chain transfer and termination is rather slow relative to the propagation at a single metal center (Fig. 5-21).  $\alpha$ -Olefins were more difficult to polymerize in a living fashion, since  $\beta$ -hydride elimination effectively competes with the insertion reaction. Furthermore, deactivation reactions such as  $\sigma$ -bond metathesis to give alkanes or the formation of a stable  $\eta^3$ -allyl complex may readily occur. Albeit with low efficiency, homogeneous Ziegler catalyst systems based on vanadi-

um(III) diketonate/ $\text{AlR}_2\text{Cl}$  were found to polymerize propylene in a living manner. Thus, at  $-78^\circ\text{C}$ ,  $\text{V}(\text{acac})_3/\text{Et}_2\text{AlCl}$  gives syndiotactic polypropylene (r dyad content 81%) with  $M_w/M_n = 1.1$  (Doi et al., 1979).

The controlled polymerization of  $\alpha$ -olefins was reported more recently using non-metallocene complexes containing linked amido-cyclopentadienyl or chelating diamido ligand systems. For example, the in situ generated 12-electron scandium complex ( $\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N-}t\text{-Bu}$ ) $\text{ScR}$  gives oligo-(propylene) at lower temperatures (Piers et al., 1990), and the Lewis acid activated diamido titanium  $\text{Ti}(\text{ArNCH}_2\text{CH}_2\text{CH}_2\text{NAr})\text{-Me}_2/\text{B}(\text{C}_6\text{F}_5)_3$  ( $\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$ ) complex has been claimed to polymerize 1-hexene even at room temperature to give poly(1-hexene) with polydispersity values as low as  $M_w/M_n = 1.05$  (Scollard and McConville, 1996). The mechanism for this polymerization, however, is not clear to date.

Regardless of the catalyst nature, once the active center is formed, chain growth proceeds by repetitive insertion of the monomer into the metal-carbon bond until chain termination by  $\beta$ -hydride elimination or chain transfer occurs. End group analysis is infor-

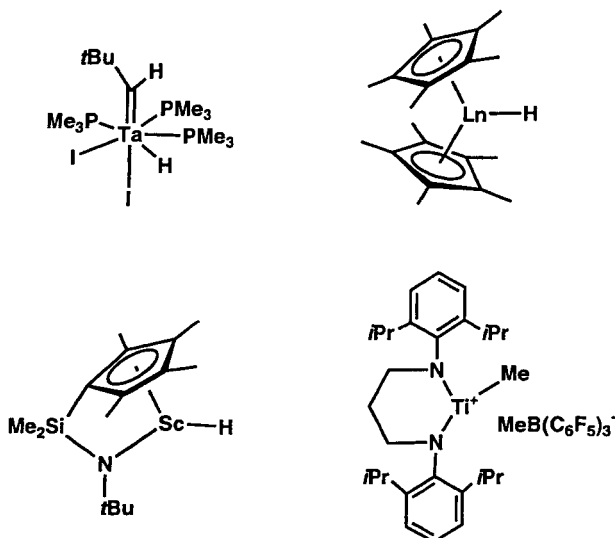


Figure 5-21. Living catalysts for olefin polymerization.

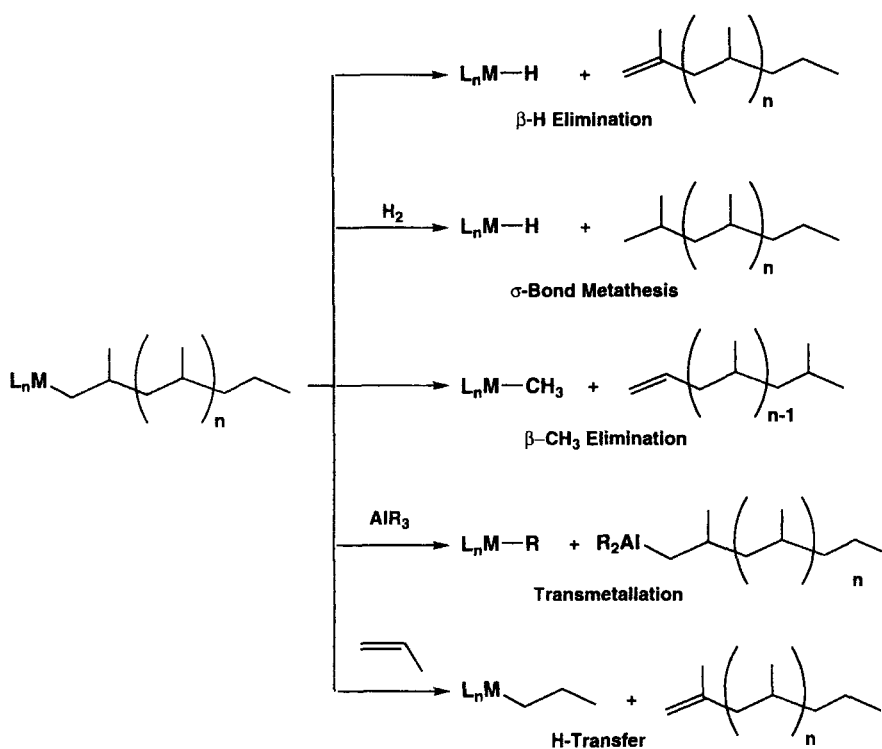


Figure 5-22. Chain termination pathways during propylene polymerization.

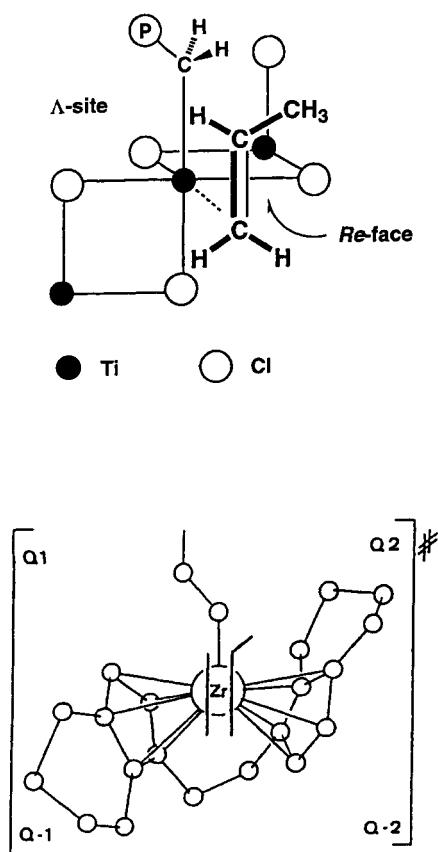
mative for determining the nature of the various termination steps, as summarized in Fig. 5-22.

The metal hydride species resulting from termination reactions, such as  $\beta$ -hydride elimination, is capable of starting a new chain. The orientation of the incoming monomer at the active center is well established using the quadrant model proposed by Pino et al. (1987) for the chiral Brintzinger-type ansa-metallocene. It is now possible to control the activity to a certain extent by manipulating the substitution pattern of the metallocene catalyst. For example, a methyl group in the 2-position of a dimethylsilyl-bridged bis(cyclopentadienyl) ligand evidently decreases the probability of chain termination. Thus, at 50 °C,  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$  gives  $M_w = 1-500$ , which is increased by  $\text{C}_2\text{H}_4(1\text{-indenyl})_2\text{ZrCl}_2$  to

$M_w = 50\,000$ , and the optimized catalyst based on the benzindenyl ligand gives  $M_w = 100\,000-500\,000$  (vide infra). The metallocene active site, as depicted in Fig. 5-23, clearly resembles the highly isospecific titanium center on the  $\alpha\text{-TiCl}_3$  surface, which through the support environment basically exerts the same steric control on the monomer.

#### 5.4.2 Regio- and Stereoselective Polymerization of $\alpha$ -Olefins

During metal-catalyzed polymerization of  $\alpha$ -olefins, the regioselectivity becomes an important issue (Fig. 5-24). If the 1-position (tail) of the 1-alkene is inserted, 1,2- or primary insertion results, which is the normal case in most of the heterogeneous and homogeneous catalysts. If the 2-posi-



**Figure 5-23.** Chiral metal sites on  $\alpha$ - $\text{TiCl}_3$  and within the  $\text{C}_2\text{H}_4(\eta^5\text{-C}_9\text{H}_{10})_2\text{Zr}$  fragment.

tion (head) of the 1-alkene is inserted, 2,1- or secondary insertion occurs. Regioirregularities such as head-to-head coupling (2,1- followed by 1,2-insertion) and tail-to-tail coupling (1,2- followed by 2,1-insertion) may occasionally occur during propylene polymerization and can be detected by defects along the polymer chain. If a (relatively slow) 2,1-insertion is followed by  $\beta$ -H elimination from the methyl group and 1,2-reinsertion and insertion of the next monomer, again in a 1,2-fashion, the polymer will exhibit a so-called 1,3-insertion with a tetramethylene segment within the chain. The polymer formed in this scenario is equivalent to a poly(propylene-co-ethy-

lene), but one that is formed from propylene without using ethylene (Fig. 5-25).

The state-of-the-art Ziegler–Natta catalysts supported on magnesium chloride were optimized to produce highly isotactic polypropylene containing less than 1% steric irregularities, such as head-to-head enchainment and isolated steric inversions due to false insertion. It is well established that chiral, catalytically active centers in the case of stereoselective supported catalysts, or the stereogenic carbon of the last monomer unit at the chain end, control enantiofacial discrimination of the prochiral  $\alpha$ -olefins. This results in stereoregular poly( $\alpha$ -olefins), while the insertion type is closely associated with the nature of the end groups and the regioselectivity.  $^{13}\text{C}$  NMR spectroscopic analysis of the polymer microstructure allows the evaluation of stereoregularity as a measure of stereoselectivity, and head-to-head enchainment as a measure of regioselectivity (Pino and Mülhaupt, 1980).

Using metallocene catalysts, the stereochemical course of the  $\alpha$ -olefin insertion has now been well established: the *cis* addition of the prochiral 1-alkene across the metal–carbon bond during the insertion is proven by the polymerization of *cis*-1,2-dideuteriopropylene- $\text{d}_5$ . According to Fig. 5-26, exclusive formation of erythro – rather than of threo diisotactic polypropylene is observed.

Depending on from which enantioface (Si or Re) each insertion occurs, three possibilities result, namely, isotactic (same enantioface, same absolute configurations along the chain), syndiotactic (alternating enantioface and absolute configurations along the chain), and atactic (random enantioface and absolute configurations along the chain). Enantiomorphic site control is operative whenever the chiral metal center discriminates between the two enantiofaces of the prochiral monomer. The chirally arranged

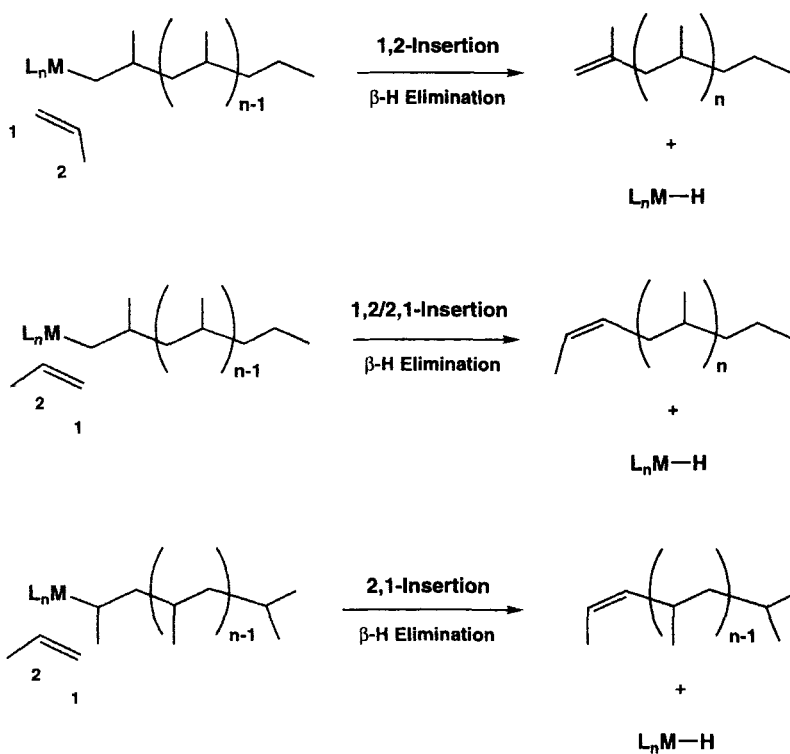


Figure 5-24. Regioselectivity of propylene insertion.

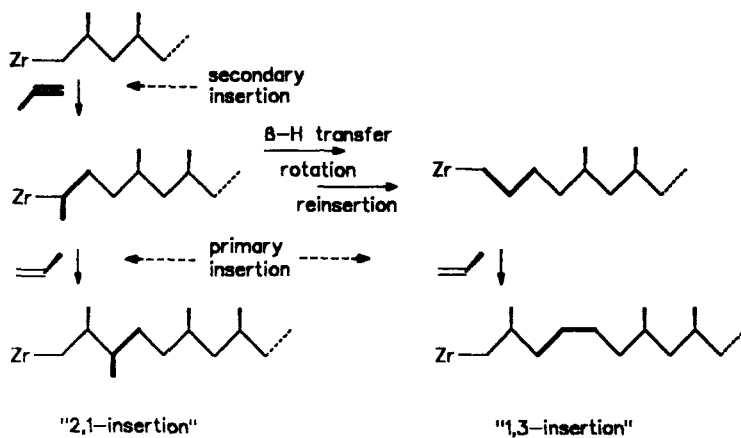


Figure 5-25. Mechanism of "1,3-insertion".

coordination sphere around the metal center is thus responsible for the stereoregularity of the poly(1-alkene). On the other hand, a so-called chain-end mechanism is operative if the stereogenic carbon atom of the

last-inserted monomer in the growing chain directs the prochiral monomer (Fig. 5-27). Ideally, by  $^{13}\text{C}$  NMR spectroscopic analyses of the methyl groups in the resulting polymer, it is possible to distinguish

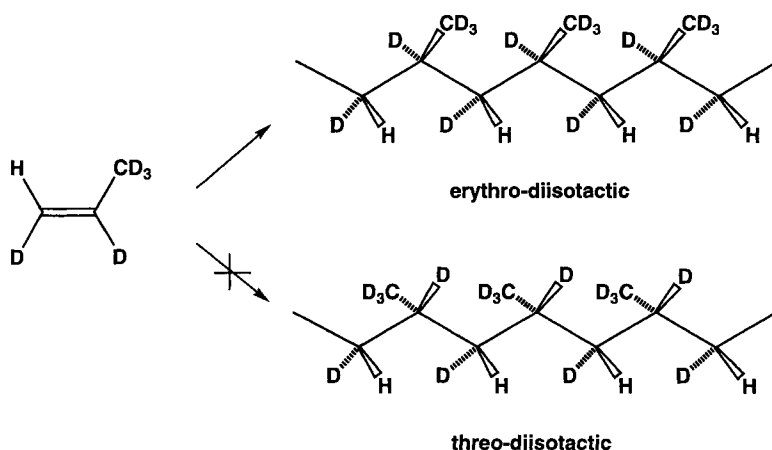
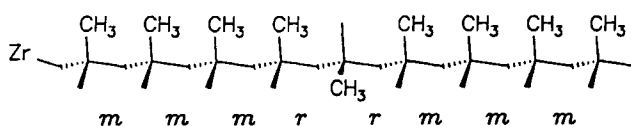


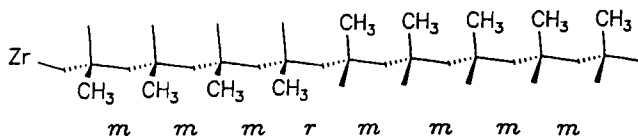
Figure 5-26. Proof of cis-insertion of propylene using (*E*)-propylene-1,2,3,3,3- $d_5$ .

Catalytic-site control



$$mmmr : \underline{mmrr} : mrmr : \underline{mrrm} = 2 : 2 : 0 : 1$$

Chain-end control



$$mmmr : mmrr : \underline{mrmr} : mrrm = 1 : 0 : 1 : 0$$

Figure 5-27. Chain end versus enantiomorphic site control.

between these two possibilities. In the case of chain end control, the error is propagated and can be detected by the presence of *mmmr* and *mrmr* pentads in a 1 : 1 ratio. If the catalyst site controls the insertion stereochemistry, any error which may occur during the propagation is “corrected”. This

can be observed by a characteristic 2 : 2 : 1 pattern of *mmmr*, *mmrr*, and *mrmr* pentads (Fig. 5-28).

With metallocene catalysts it has become possible to tailor various catalysts and to produce almost at will a broad range of stereoisomeric polypropylenes, as summar-





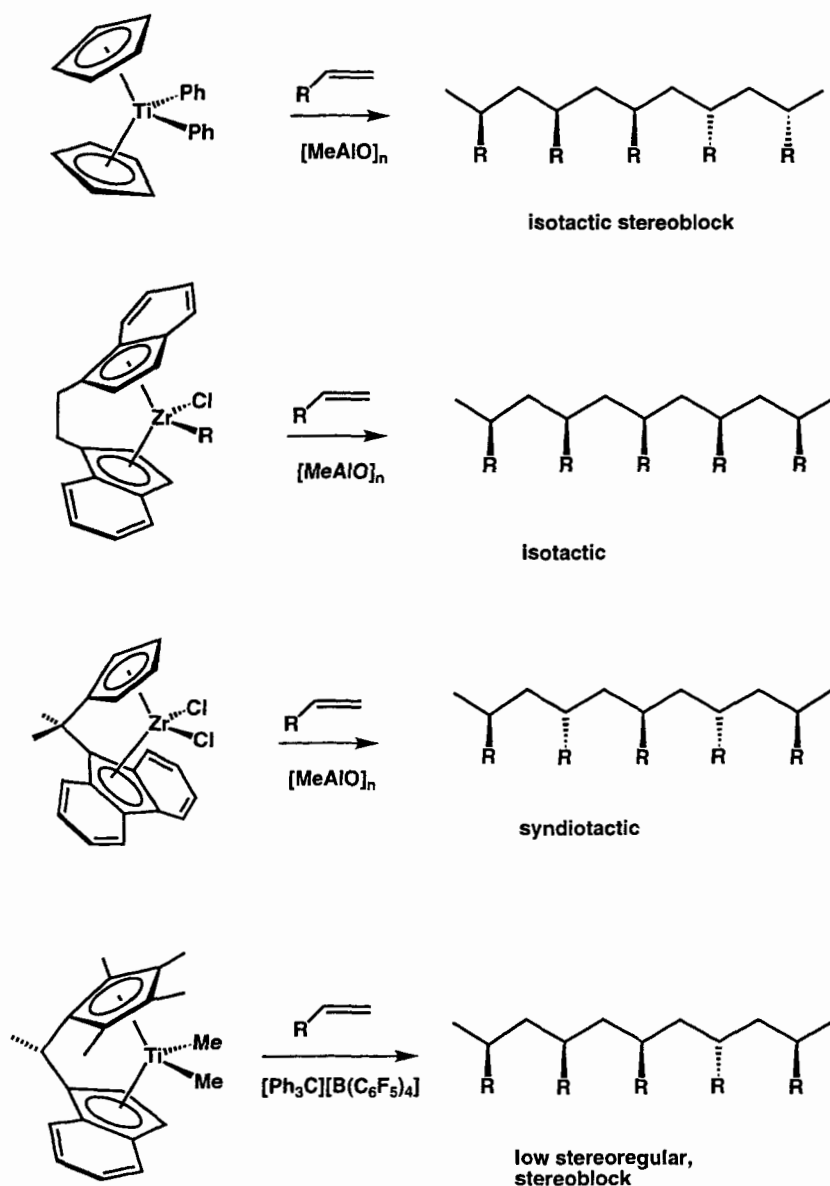
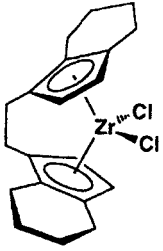
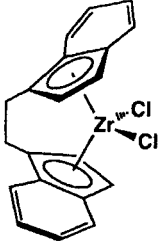
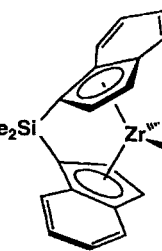


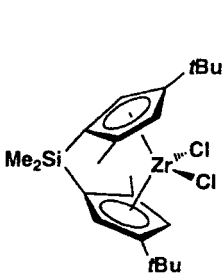
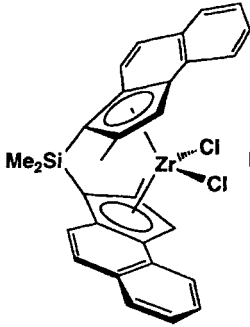
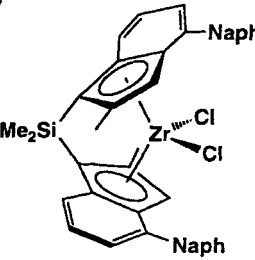
Figure 5-29. Polypropylene by metallocene catalysis.

lute configuration of the metal center alternates (Fig. 5-31). Unless the chain does not migrate to the other side (back skip), the next incoming monomer always approaches the metal from the opposite side, resulting in the formation of syndiotactic polypropylene with alternating absolute config-

urations of the stereogenic carbon atom in the monomeric repeat units. Such fluorenyl-based metallocene catalysts produce syndiotactic polypropylene in high yields and are currently being considered for commercial scale-ups, since this polypropylene exhibits higher toughness and improved opti-

			
$10^{-3}M_w$	15	24	36
% mmmm	85	78.5	81.7
$T_m, ^\circ\text{C}$	125	132	137

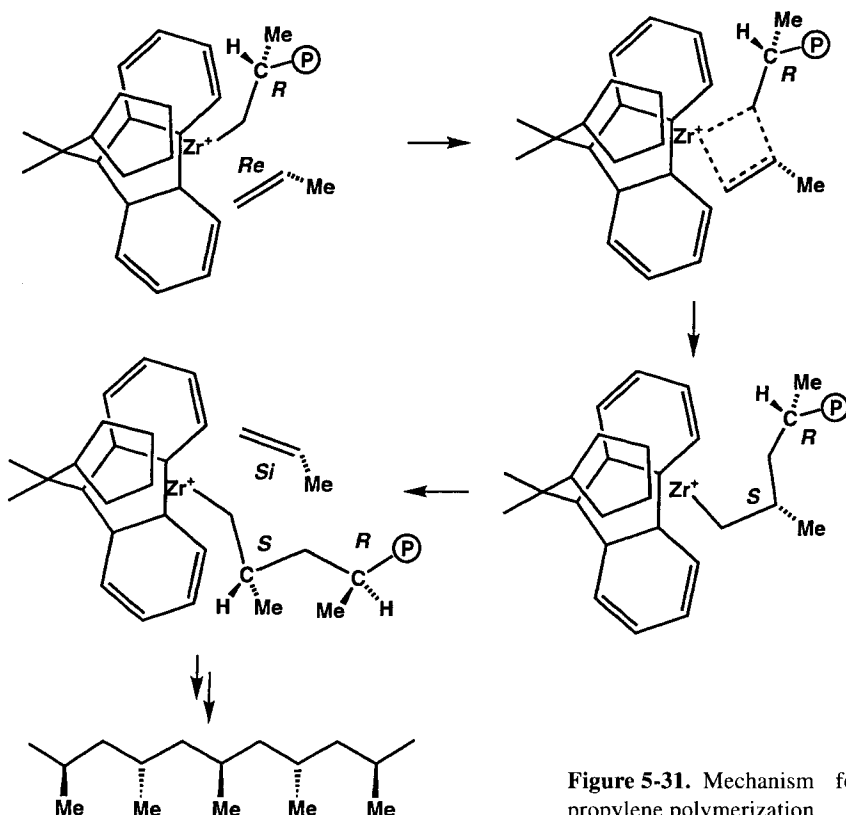
			
$10^{-3}M_w$	19	330	875
% mmmm	94.3	88.7	99.1
$T_m, ^\circ\text{C}$	155	146	161

**Figure 5-30.** Evolution of highly isospecific metallocene catalyst. Polymerization conditions: Al: Zr = 150 000; 70 °C in liquid propylene (Spaleck et al., 1994).

cal clarity with slightly reduced hardness and stiffness. Syndiospecific polymerization of propylene could only be performed with low efficiency at  $-78^\circ\text{C}$  using the classic Ziegler catalyst system  $\text{VCl}_4/\text{AlEt}_2\text{Cl}$ . In this case 2,1-insertion of propylene occurs predominantly and chain-end control seems to determine the syndiospecificity.

The correctness of the mechanistic interpretation for stereospecific metallocene catalysts was corroborated by the development

of hemiisotactic and isotactic polypropylenes by merely increasing the steric bulk of the cyclopentadienyl ligand by introducing a methyl and *tert*-butyl substituent in the 3-position within the isopropylidene bridged (cyclopentadienyl)(9-fluorenyl) ligand framework (Fig. 5-32). More recently, the first nonfluorenyl-based metallocene catalysts  $(\text{Me}_2\text{Si})_2(\eta^5\text{-C}_5\text{H}_2\text{R})(\eta^5\text{-C}_5\text{-}i\text{-Pr}_2\text{H})\text{ZrCl}_2$  for syndiospecific polymerization were developed; these also allow a

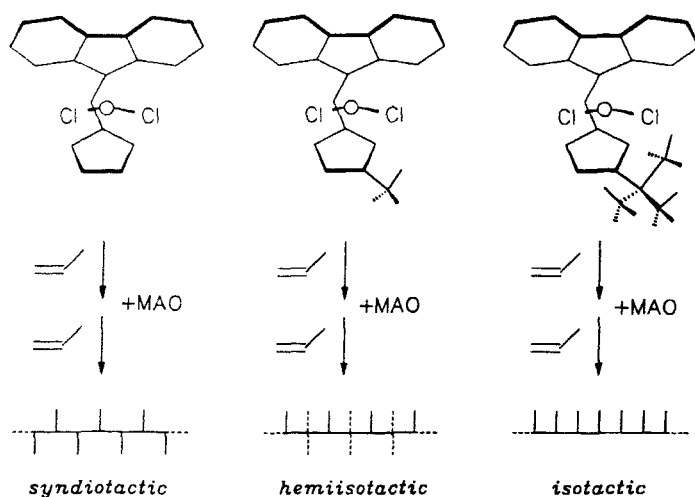


**Figure 5-31.** Mechanism for the syndiospecific propylene polymerization.

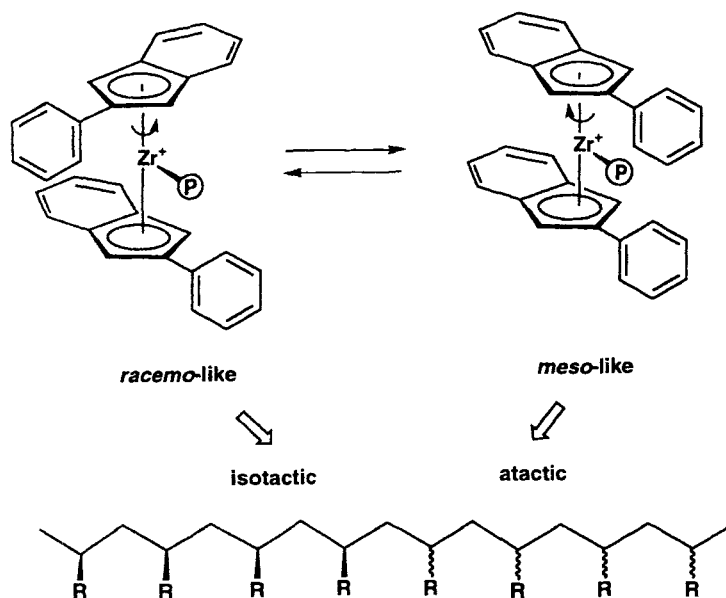
switch of the stereoselectivity by modifying R (Herzog et al., 1996).

Stereoblock copolymers containing crystalline isotactic segments and highly flexible amorphous, less stereoregular segments form thermally reversible, crosslinked, melt-processable elastomers. According to Chien (Llinas et al., 1992), the methylaluminumoxane-activated, ethylidene-bridged tetramethylcyclopentadienyl indenyl derivative  $\text{MeHC}(\eta^5\text{-C}_5\text{Me}_4)(\eta^5\text{-C}_9\text{H}_6)\text{TiCl}_2$  produces thermoplastic elastomeric polypropylenes exhibiting high elongation, low modulus, and mechanical hysteresis. Earlier heterogeneous multi-site systems,  $\text{Zr}(\text{CH}_2\text{CMe}_2\text{Ph})_4/\text{alumina}$ , were reported to form in situ blends of isotactic and stereoblock polypropylenes. So-called oscillating catalysts introduced by Waymouth and

Coates (1995) consist of nonlinked metallocene complexes such as bis(2-phenylindenyl)zirconium dichloride. Upon activation with methylaluminumoxane, it is capable of producing stereoblock polypropylene with both isotactic and atactic segments, depending on the monomer concentration and temperature. The mechanism proposed implies the presence of rotational isomers of racemo-like and meso-like conformations, which result from the hindered rotation of the substituted indenyl ligands about the metal–ligand axis. The  $C_2$ -symmetric conformation is believed to give rise to isospecificity, while the meso-like conformation results in aspecific monomer insertions (Fig. 5-33). Methylaluminumoxane-activated bis(1-methylfluorenyl)zirconium dichloride gives at 60 °C polypropylene with 83%



**Figure 5-32.** Metallocene catalysts for syndiotactic, hemiisotactic, and isotactic polypropylene.



**Figure 5-33.** "Oscillating" metallocene catalysts for propylene polymerization.

mmmm pentad distribution, suggesting that the chiral  $C_2$ -symmetry is retained and the ligand rotation is prohibited (Razavi and Atwood, 1993). Metallocene catalysts without bridges have attracted some interest as synthetically easier accessible alternatives for the isospecific ansa-metallocenes, but the loss of stereorigidity normally gives a more flexible catalyst which is better suited for the synthesis of stereoblock polyolefins.

### 5.4.3 Polymerization of Cyclic Olefins, Cyclopolymerization, and Stereoselective Polymerization of Styrene

Strained unsaturated alicycles have been known to be polymerizable by a number of structurally well-characterized organometallic complexes under ring opening olefin metathesis polymerization (ROMP). On the other hand, some Ziegler catalysts induce

the polymerization of such monomers without ring opening. ansa-Metallocenes were found to polymerize cyclobutene, cyclopentene, and norbornene to give materials with very high heat distortion temperatures. Cyclopentene undergoes a remarkable isomerization within the coordination sphere and gives a polymer with strictly 1,3- instead of 1,2-enchainment (Collins and Kelly, 1992). Depending on the metallocene structure, both *cis* and *trans* configuration of the 1,3-cyclopentanediyl units can be observed (Fig. 5-34). On the other hand, norbornene was found to be polymerized to give poly(norbornene) by *cis*-*exo* 1,2-insertions. From the commercial standpoint, metallocene-catalyzed copolymerization of ethylene with cyclopentene and norbornene has attracted major interest (see Sec. 5.5).

Although optically active oligomers can be obtained in the presence of a resolved chiral metallocene complex, high molecular weight isotactic, as well as syndiotactic, polypropylene contain mirror planes and are therefore achiral ("cryptochiral"). Coates and Waymouth (1993) employed the ho-

mogeneously catalyzed cyclopolymerization of 1,5-hexadiene giving poly(methylene-1,3-cyclopentane) in order to utilize the stereoselectivity of the monomer insertion for the construction of a polymer with main chain chirality. Cyclopolymerization is a chain growth reaction during which a conventional insertion of a vinylic function into the transition metal-carbon bond is followed by an intramolecular insertion, resulting in the formation of alicyclic rings connected by methylene groups. Thus, from 1,5-hexadiene, a polymer chain is obtained in which methylene and 1,3-cyclopentanediyl fragments are arranged in a strictly alternating sequence (Fig. 5-35). By modifying the catalyst's ligand sphere, control over the diastereoselectivity could be achieved:  $\text{Cp}_2\text{ZrCl}_2$  leads to mainly *trans*, the sterically more congested  $\text{Cp}^*\text{ZrCl}_2$  predominantly to *cis*, connection of the cyclopentane fragments. An analysis of possible stereoisomers shows four structures of maximum order, of which all but the racemo-diisotactic polymer are achiral. The latter does not contain a mirror plane and is chiral due to

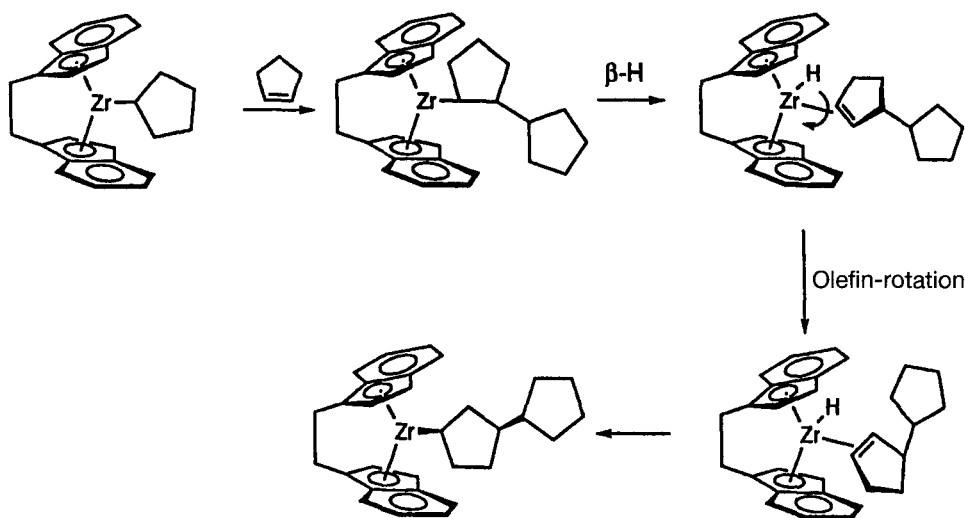
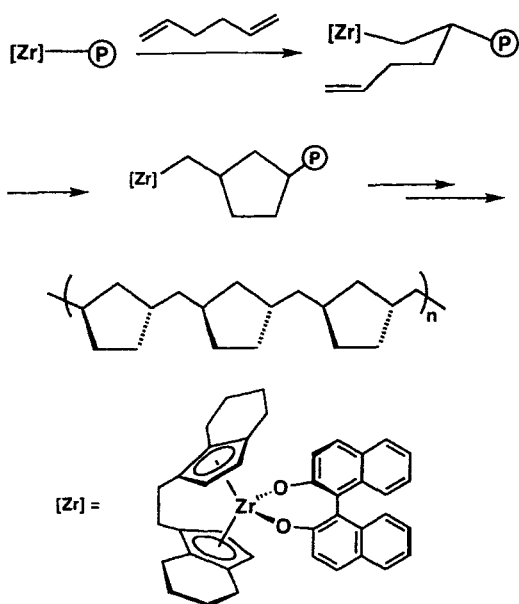
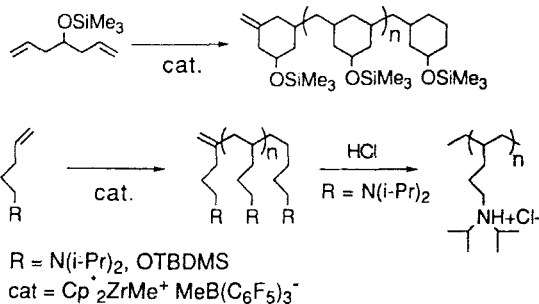


Figure 5-34. 1,3-Enchainment of cyclopentene.



**Figure 5-35.** Enantioselective cyclopolymerization of 1,5-hexadiene.



**Figure 5-36.** Cyclopolymerization of functionalized 1,6-heptadiene.

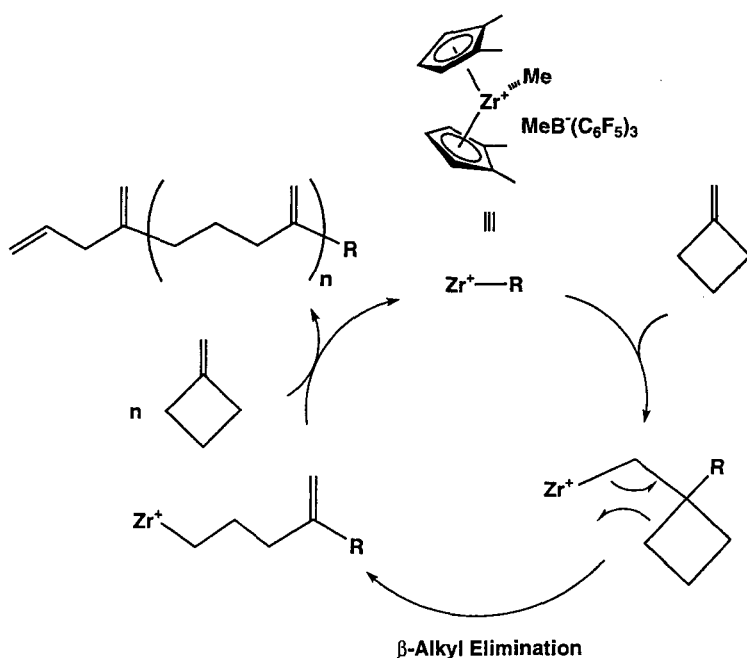
configurationally determined main chain stereochemistry. By using a chiral catalyst [1,1'-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium, 1,1'-binaphtholate, which had been prepared from optically active (*R*)- or (*S*)-1,1'-binaphthol, the enantioselective cyclopolymerization of 1,5-hexadiene was in fact possible. Poly(methylene-1,3-cyclopentane) synthesized in the presence of (–)-(*R,R*)-enantiomer and methylalumox-

ane revealed a molar optical rotation of  $[\Phi]^{28405} = +51.0^\circ$ , whereas the polymer analogously prepared using the (+)-(*S,S*)-enantiomer showed a value of  $[\Phi]^{28405} = -51.2^\circ$ , consistent with the formation of polymers with main chain chirality (Fig. 5-35).

Cyclopolymerizations of functionalized 1,6-heptadienes such as 4-trimethylsiloxy-1,6-heptadiene became possible using  $\text{Cp}^*_2\text{ZrCl}_2$  and  $\text{B}(\text{C}_6\text{F}_5)_3$  as the cocatalyst (Fig. 5-36). Upon hydrolysis, poly(methylene-3-hydroxycyclohexane) is obtained (Kesti et al., 1992).

Methylenecyclobutane can be polymerized using  $(\eta^5\text{-}1,2\text{-Me}_2\text{C}_5\text{H}_3)_2\text{ZrMe}_2/\text{B}(\text{C}_6\text{F}_5)_3$  to give a new type of polyolefin with methylene groups along the main chain. The proposed mechanism implies the 1,2-insertion of one monomer and a  $\beta$ -alkyl isomerization to give an alkyl intermediate followed by the next insertion (Fig. 5-37). The formation of the ring-opened polymer by direct oxidative addition of the 2–3 bond of the methylenecyclobutane was ruled out since copolymerization with excess  $^{13}\text{C}$ -labeled ethylene results in a copolymer where every  $\text{CH}_2$  group is flanked by one  $^{13}\text{CH}_2$  and one  $^{12}\text{CH}_2$  unit. According to kinetic studies, the monomer insertion and not the ring opening is the turnover-limiting step (Yang et al., 1993).

When soluble titanium complexes are activated with methylaluminoxane or by any of the protocols to prepare the titanium-centered alkyl cations, styrene is polymerized to give syndiospecific polystyrene (Ishihara et al., 1988; Po and Cardi, 1996). In contrast to amorphous atactic and also isotactic polystyrene, previously prepared by classical Ziegler catalysts  $\text{TiCl}_4/\text{AlEt}_3$ , and easily discerned by NMR spectroscopy (Fig. 5-38), syndiotactic polystyrene is a potentially useful material. It shows a remarkably high melting temperature of about



**Figure 5-37.** Polymerization of methylenecyclobutane.

270 °C (isotactic polystyrene:  $T_m = 224$  °C) and high crystallinity along with a good rate of crystallization. It is resistant to chemicals, steam, and electric and mechanical stress, and is expected to become a new engineering plastic. The crystal structure of syndiospecific polystyrene has been studied in much detail and the different modifications analyzed in terms of its chain conformations (zigzag chain versus  $2_1$ -helix).

Since the original discovery by Ishihara et al. in 1985, it has been recognized that mono(cyclopentadienyl)titanium complexes of the general type  $(\eta^5\text{-C}_5\text{R}_5)\text{TiX}_3$  are the most efficient catalysts when activated with methylaluminoxane (Fig. 5-39). Despite many contradictory and inconsistent claims, the most reasonable model for the catalytically active species to date implies a cationic Ti(III) alkyl of the type  $[(\eta^5\text{-C}_5\text{R}_5)\text{TiR}]^+$ , which is formed in the reaction mixture. This presumably exceedingly sensitive species, so far detected by ESR spectroscopy, results from the initial cationic species

of tetravalent titanium  $[(\eta^5\text{-C}_5\text{R}_5)_2\text{TiR}_2]^+$ , which undergoes homolytic cleavage of one of the two alkyl groups. The observation that other metal centers, including the homologous zirconium as well as bis(cyclopentadienyl)titanium complexes, are far less active, supports this activation mechanism, which is fundamentally different from the usual “metallocene catalysis” involving cationic alkyl species of tetravalent metal centers. One of the requirements for a catalyst to be able to polymerize styrene stereoselectively, apart from being a cationic alkyl (or hydride) species, is the presence of one sterically demanding ligand such as pentamethylcyclopentadienyl. However, Ti(II) species containing a neutral arene ligand (including styrene) may be another choice, which would explain the activity of simple titanium alkoxides such as  $\text{Ti}(\text{OPh})_4$  (Zambelli et al., 1991). The chain propagation occurs by secondary insertion, i.e., the benzylic carbon is attached to the metal center, and cis opening of the double bond was demon-



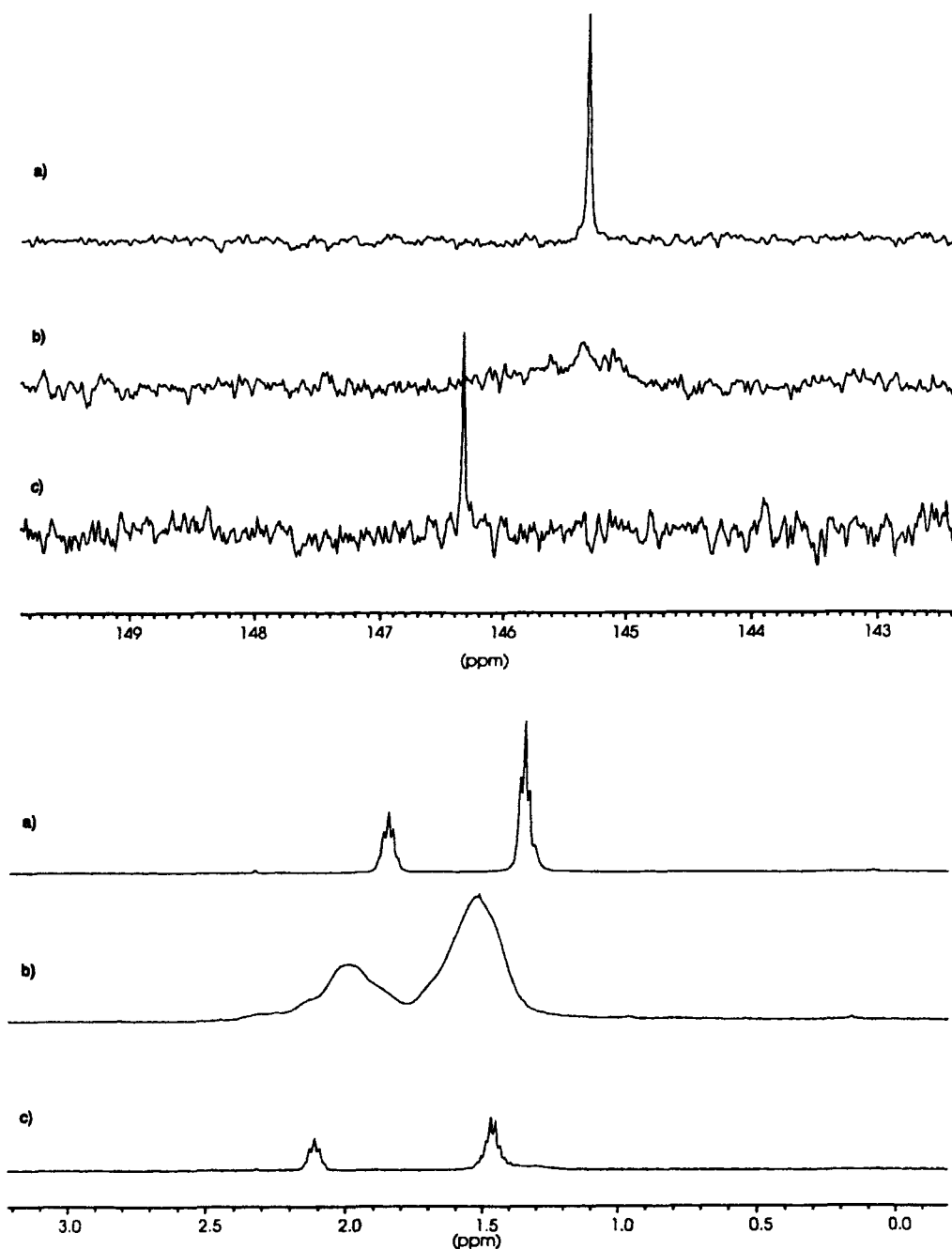
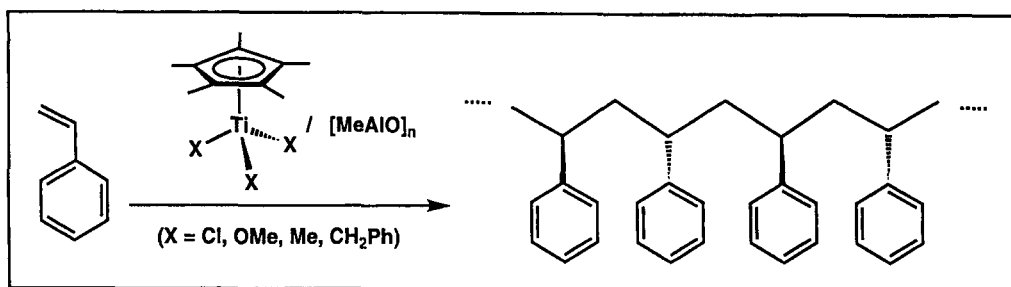


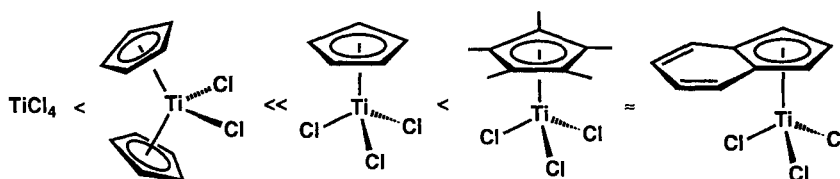
Figure 5-38.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of (a) syndiotactic, (b) atactic, and (c) isotactic polystyrene.

strated in analogy to the metallocene catalysts for  $\alpha$ -olefins (vide supra). The extremely high stereoselectivity usually ob-

served (>90%; isolated m dyads) can be rationalized by a 1,3-asymmetric induction, caused by repulsive interactions of the in-



#### Relative Order of Activity



#### Transition State Model

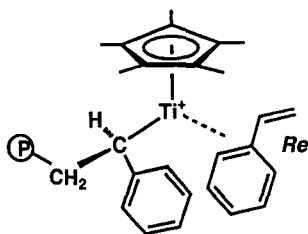


Figure 5-39. Syndiospecific polymerization of styrene.

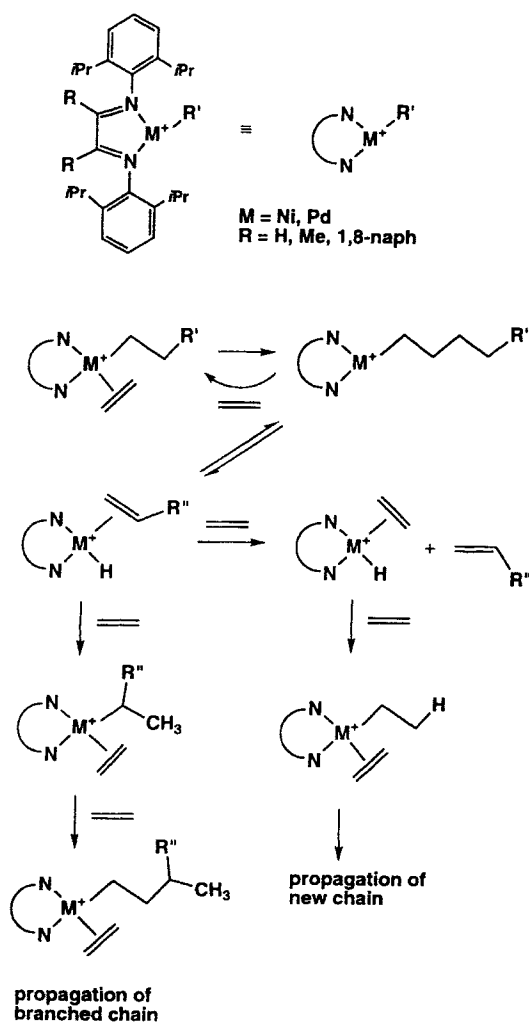
coming styrene monomer and the phenyl group at the stereogenic carbon of the last-inserted styrene.

Conjugated 1,3-dienes can also be polymerized by mono(cyclopentadieny)titanium complexes such as  $\text{CpTiCl}_3/\text{MAO}$  to give mainly *cis*-1,2-polydienes, but a strong dependence of the stereoselectivity on the polymerization conditions has been noted (Ricci et al., 1995).

#### 5.4.4 Late Transition Metal Catalysts

Nickel catalysts for ethylene oligomerization, such as the ones used commercially in the SHOP process, can be modified by

ligand exchange to become active for ethylene polymerization (Klabunde and Mülhaupt, 1987). In particular, nickel complexes containing phosphorus ylides  $\text{R}_3\text{P}=\text{CH}_2$  as the controlling ligands proved to be active, forming polyethylene with a molecular weight up to  $10^6$  (Ostoja-Starzewski and Witte, 1987). Recently, nickel and palladium complexes of 1,2-diimine ligands of the type  $\text{M}(\text{ArN}=\text{C}(\text{R})\text{C}(\text{R})=\text{NAr})\text{Br}_2$  ( $\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$ ,  $\text{R} = \text{H}$ , Me, 1,8-naph) were reported as a new class of structurally well-defined olefin polymerization catalysts, when activated with methylaluminumoxane (Johnson et al., 1995). The active species appear to be tricoordinate 14-electron alkyl cations  $[\text{M}(\text{ArN}=\text{C}(\text{R})\text{C}(\text{R})=\text{NAr})\text{R}]^+$ , quite similar to the metallocenium ions described above for the group 4 metallocene dichlorides. For  $\text{M} = \text{Pd}$ , detailed studies were carried out on the structure and dynamic behavior of the cation. When nickel derivatives were used, both highly linear and new types of branched polyethylenes with predominantly methyl groups were obtained. The branching is a function of the catalyst structure as well as



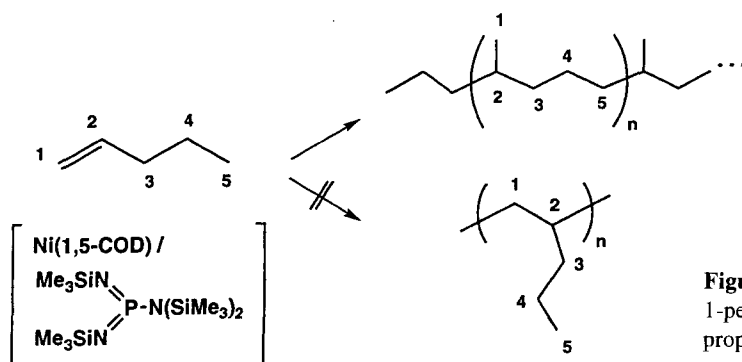
**Figure 5-40.** Ethylene polymerization by nickel and palladium complexes with 1,2-diimine ligands.

the temperature and monomer concentration. At lower temperatures, highly branched polymer is obtained, whereas at higher ethylene pressure or by using smaller aryl substituents, linear polymer is formed. According to Fig. 5-40, the resting state of the catalyst is an ethylene alkyl cation which can undergo insertion followed by  $\beta$ -hydride elimination, resulting in the formation of an olefin hydride complex. 2,1-Insertion of the olefin into the nickel hydride

bond gives a secondary alkyl group. Complexation of ethylene and further insertion produce a methyl branch, while further chain migration via  $\beta$ -hydride elimination and readdition processes lead to longer branches.

When 1-alkenes such as propylene and 1-hexene are polymerized using this type of catalyst, the resulting poly(1-alkene)s exhibit fewer branches than theoretically expected in polymers where chain growth occurs exclusively by 1,2-insertions [polypropylene: 330  $\text{CH}_3$  groups per 100 carbon atoms; poly(1-hexene): 167  $\text{CH}_3$  groups per 1000 carbon atoms]. This phenomenon was coined "chain straightening" and can be accounted for by assuming a mechanism with extensive chain migration. Fink and Möhring (1985) had previously developed an interesting, novel approach to incorporate methyl short chain branches into polyethylene chains. A catalyst system made from nickel (0) complexes such as  $\text{Ni}(1,5\text{-COD})$  or  $\text{Ni}(1,5,9\text{-CDT})$  ( $\text{COD}$  = cyclooctadiene,  $\text{CDT}$  = cyclododecatriene) and bis(trimethylsilyl)aminobis(trimethylsilyl)phosphorane polymerizes 1-pentene to give strictly alternating poly(ethene-*alt*-propene) with exclusive methyl side chains. This remarkable  $2\omega$ -polymerization is attributed to the migration of nickel alkyls (Fig. 5-41).

Finally, cationic palladium complexes of the type  $(\text{PdL}_4)^{2+}$ , recognized as the active species for the copolymerization of olefins with carbon monoxide (see Sec. 5.5), polymerize strained cyclic olefins such as 3,3-dialkylcyclopropene and norbornene without ring opening (Rush et al., 1996). Related cationic nickel catalysts  $[\text{Ni}(1,5\text{-COD})(\eta^3\text{-C}_3\text{H}_5)]^+$  are presently being commercialized by B. F. Goodrich for the polymerization of norbornene to give novel saturated glassy polymers.



**Figure 5-41.** 2, $\omega$ -Polymerization of 1-pentene to give poly(ethylene-*alt*-propene).

## 5.5 Transition Metal Catalyzed Copolymerization

Tailoring polyolefin materials frequently involves transition metal catalyzed olefin copolymerization in single or multi-staged reactors. According to Fig. 5-42, the copolymerization of ethylene (E) and propylene (P) can afford random, alternating, or segmented copolymers. Based on the 1-olefin comonomer content, there are several classes of semi-crystalline, amorphous, flexible, and rubbery materials in the ethylene copolymer family, which are classified according to their comonomer content (Table 5-1).

Many of the traditional Ziegler-Natta and Phillips catalysts are composed of different active sites with greatly varied reactivity towards comonomer incorporation. Frequently, the comonomer was incorporated into the low molecular weight, wax-like fractions, which caused tackiness of the resulting polymer and migration problems in packaging applications. Therefore such multi-site catalysts produced very heterogeneous ethylene copolymers containing homopolymer, as well as waxes. In the absence of multipurpose catalyst systems, specific systems were developed for HDPE, LLDPE, EPM, and polypropylene production. VLDPE and plastomers were not available with conventional catalyst systems. This situation

poly(ethene-*co*-propene)

-EEEEPEEPPPEEPEEPPP- random  
-EPEPEPEPEPEPEPEPE- alternating  
-EEEEEE-PPPPPP-EEEE- block

**Figure 5-42.** Sequence distribution of poly(ethylene-*co*-propylene).

**Table 5-1.** Classification of ethylene copolymer family according to the comonomer content

Comonomer content	Copolymer type
0%	high density polyethylene (density 0.96 g/cm <sup>3</sup> )
0 – 5%	linear low density polyethylene (density 0.91 – 0.96 g/cm <sup>3</sup> )
5 – 15%	very low density polyethylene (density 0.88 – 0.91 g/cm <sup>3</sup> )
15 – 40%	amorphous, flexible plastomers
40 – 70%	amorphous rubbers
70 – 99%	impact-modified poly(1-olefin)s
100%	poly(1-olefin), e.g., polypropylene

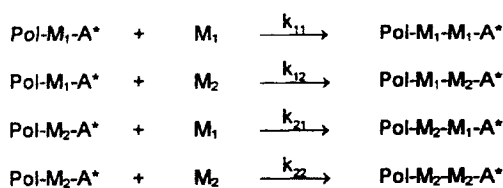
changed dramatically when single-site metallocenes were developed during the late 1980s. With metallocene catalysts it became possible to vary the comonomer compositions over the entire composition range without sacrificing high molecular mass and uniform comonomer incorporation (Mülhaupt, 1996). VLDPE and plastomers, as well as a wide range of oligomers, were

introduced commercially during the 1990s. VLDPE exhibits much higher impact strength and significantly higher optical transparency, because polyethylene homopolymer impurities are not formed as by-products. Random incorporation of more than 20% 1-octene comonomer gave plasomers that crystallized to form fringed micelle nanostructures. Also, EPM and EPDM were improved with respect to their homogeneity.

According to Markovian first-order statistics, the incorporation of two monomers can be described using two copolymerization parameters  $r_1$  and  $r_2$ . The copolymerization parameter  $r_1$  is equivalent to the ratio of the propagation rate constant for in-

sertion of monomer 1 or monomer 2 after inserting monomer 1 (see Fig. 5-43). Copolymerization parameters can be determined by the method of Mayo and Lewis (1994) at low conversion using different monomer feed ratios and analyzing the effect of this feed ratio on the comonomer content of the resulting copolymer. According to Uozumi and Soga (1992), NMR spectroscopic analysis of dyad distribution, taking into account the monomer concentration, can be applied to determine the  $r$ -parameters from only one copolymerization experiment.

The sequence distribution of copolymers can be evaluated with  $r_1 r_2 \gg 0$  for block copolymers or mixtures with homopolymers,  $r_1 r_2 = 0$  for alternating copolymers, and  $r_1 r_2 = 1$  for random copolymers (see Fig. 5-42). Typical copolymerization parameters are listed in Table 5-2 for various catalyst systems. Most conventional  $\text{TiCl}_3$ -based catalyst systems exhibit large copolymerization parameters  $r_E$  and  $r_E r_P > 1$ , which is typical for predominant ethylene homopolymerization. Therefore special vanadium catalysts have been developed to produce poly(ethene-*co*-propene) rubbers. With metallocene catalysts, the copolymer-

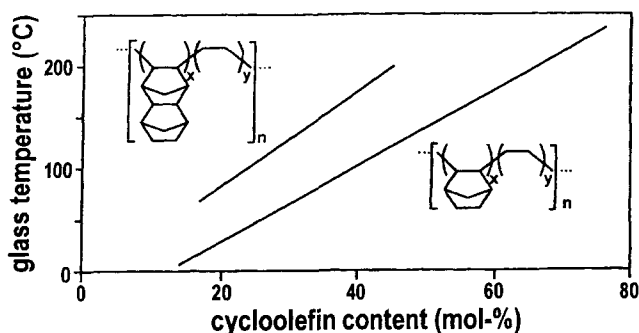


**copolymerization parameters**  $r_1 = k_{11}/k_{12}$ ;  $r_2 = k_{22}/k_{21}$

**Figure 5-43.** First order Markovian statistics of binary copolymers.

**Table 5-2.** Copolymerization parameters for various metallocene catalysts of ethylene and 1-alkenes. Ethene/1-olefin copolymerization

Catalyst system	1-Olefin	$r_E$	$r_P$	$r_O$	$r_1 r_2$
$\text{TiCl}_3/\text{AlEt}_2\text{Cl}$	propene	24	0.10		2.5
$\text{MgCl}_2/\text{EB}/\text{TiCl}_4/\text{AlEt}_3^a$	propene	13.4	0.40		5.4
$\text{VCl}_3/\text{AlEt}_2\text{Cl}$	propene	5.9	0.029		0.14
$(\text{Me}_5\text{Cp})_2\text{ZrCl}_2/\text{MAO}$	propene	250	0.002		0.50
$\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$	propene	16.6	0.06		0.40
$\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2/\text{MAO}$	propene	1.3	0.20		0.26
$\text{Me}_2\text{Si}(\text{Me}_2\text{Cp})(\text{N}^i\text{Bu})\text{TiCl}_2/\text{MAO}$	1-octene	4.1		0.290	1.19
$\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$	1-octene	18.9		0.014	0.27
$\text{Me}_2\text{Si}(2\text{-Me-Ind})_2\text{ZrCl}_2/\text{MAO}$	1-octene	19.5		0.013	0.25
$\text{Me}_2\text{Si}(\text{Benz-Ind})_2\text{ZrCl}_2/\text{MAO}$	1-octene	10.7		0.076	0.81
$\text{Me}_2\text{Si}(2\text{-Me-Benz-Ind})_2\text{ZrCl}_2/\text{MAO}$	1-octene	10.1		0.118	1.20
$\text{Cp}_2\text{ZrCl}_2/\text{MAO}$	1-octene	32.8		0.050	0.17



**Figure 5-44.** Glass transition temperatures for the copolymers of ethylene with norbornene.

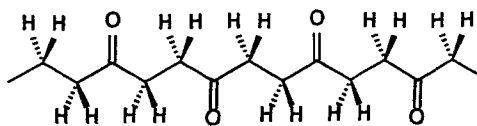
ization parameters can be varied over a very wide range as a function of the metallocene structure. While  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrCl}_2/\text{MAO}$  fails to incorporate higher 1-olefins into polyethylene chains, the half-sandwich complex  $(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{N-}t\text{-Bu})\text{TiCl}_2$ , activated with MAO, gives random incorporation of very large amounts of higher 1-olefin comonomer.

Moreover, metallocene catalysts have been tailored to manufacture random copolymers of ethylene and styrene (Sernetz et al., 1996), as well as cycloolefins such as norbornene (Cherdron et al., 1994). As a function of the metallocene catalyst structure, crystalline or amorphous random and alternating copolymers of ethylene and norbornene can be obtained. As shown in Fig. 5-44, the glass transition temperature of poly(ethylene-*co*-norbornene) increases with increasing norbornene content. High  $T_g$  cycloolefin copolymers exhibit high dimensional stability, strength, and excellent optical properties. Such materials qualify as engineering resins and medical packaging.

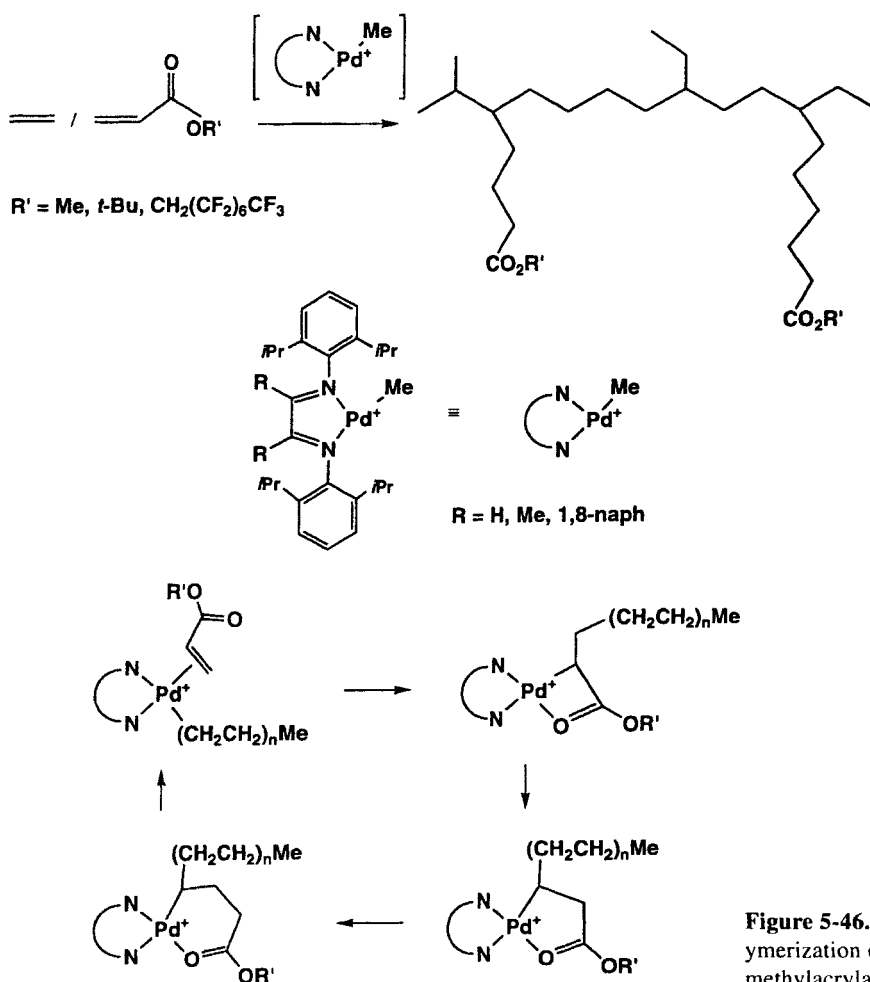
Most traditional Ziegler-Natta catalysts and metallocenes based upon group 4 transition metals are severely poisoned by Lewis bases because of the high Lewis acidity of the catalytically active transition metal sites. Recently, novel catalyst families based upon much less Lewis acidic group 8

transition metals, such as palladium and nickel, have been developed. Drent and Budzelaar (1996) described several catalyst systems which tolerate the well-known catalyst poison carbon monoxide (CO) and produce strictly alternating copolymers with ethylene (see Fig. 5-45) and various other olefins and dienes. When a few percent of propylene is present during ethylene/CO copolymerization, the resulting copolymer exhibits a melting temperature of 225 °C and properties similar to those of polyamide 6. In 1996 Shell started commercial production of such polyketones (Carillon).

1,2-Diimine complexes of nickel and palladium can be activated to form branched polyethylene derived from ethylene without adding 1-olefin comonomer (see Sec. 5.4.4) and also poly(ethylene-*co*-methylacrylate) (Brookhart et al., 1996). The chain migration mechanism, as shown in Fig. 5-40, accounts for the formation of branched polyethylene containing *n*-alkyl and  $\omega$ -carboalkoxy alkyl side chains (see Fig. 5-46). The *n*-alkyl chains result from cooligomeriza-



**Figure 5-45.** Poly(1-olefin-*alt*-CO).



tion of ethylene with methyl acrylate and simultaneous copolymerization with ethylene. The controlled formation of polar and nonpolar short chain and long chain branched ethylene copolymers opens up the attractive potential of manufacturing novel tailor-made polyolefins. The tolerance of polar comonomers in low pressure catalytic copolymerization will lead to novel low cost materials, which overcome the property limitations of the nonpolar, hydrocarbon-based polyolefins, such as lack of dyeability, adhesion, and moisture absorption.

It is now quite evident that future endeavors will be directed towards developing new families of nonmetallocene, single-site catalysts with their capability expanding to polar monomer incorporation and to even better control of the macromolecular architecture.

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## 6 Living Radical Polymerization

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## List of Symbols and Abbreviations

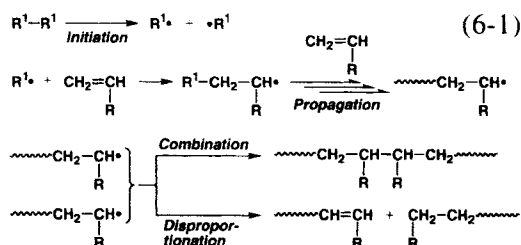
$h$	Planck constant
$K$	equilibrium constant
$k_L$	trapping rate constant
$k_P$	propagation rate constant
$k_{\text{frag}}$	fragmentation rate constant
$k_{\text{graft}}$	grafting rate constant
$l$	integer
$m$	integer
$\bar{M}_n$	mean number-average molecular weight
$\bar{M}_w$	mean weight average molecular weight
$\bar{M}_n/\bar{M}_w$	molecular weight distribution
$n$	integer
$\Delta$	heat
$\nu$	frequency
Ac	acetyl
AIBN	azobisisobutyronitrile
AN	acrylonitrile
ATRP	atom-transfer radical polymerization
BA	<i>n</i> -butyl acrylate
BMA	<i>n</i> -butyl methacrylate
BPO	benzoyl peroxide
Bu	butyl
CSA	camphorsulfonic acid
DMF	dimethylformamide
EA	ethyl acrylate
eacac	ethyl acetoacetate
ESR	electron spin resonance
Et	ethyl
FMPTS	2-fluoro-1-methylpyridinium <i>p</i> -toluene sulfonate
HMPA	hexamethylphosphoramide
L	ligand
M	metal
MA	methyl acrylate
Me	methyl
MMA	methyl methacrylate
MWD	molecular weight distribution
NMR	nuclear magnetic resonance
ODBP	2,6-di- <i>tert</i> -butyl phenoxy
Ph	phenyl
PhMA	phenyl methacrylate

PS	polystyrene
SEC	size exclusion chromatography
St	styrene
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl
TG	thermogravimetry
THF	tetrahydrofuran
TMP	tetramesitylporphyrinato
UV	ultraviolet
VAc	vinyl acetate

## 6.1 Introduction

### 6.1.1 Control of Free Radical Polymerization

Radical, or free radical, polymerization has been considered difficult to control for a long time due to the highly reactive radical intermediate that usually undergoes fast reactions with low selectivity, as in the radical reactions of small molecules (Curran et al., 1996; Moad and Solomon, 1995). The most unfavorable reaction therein is in one between the radical species themselves, which occurs much faster (often at the diffusion-controlled limit) than favorable reactions between the radical and the substrate. In conventional radical polymerizations, for example, the growing radical reacts not only with monomer to induce propagation but also with another growing radical end to terminate the propagation via combination or disproportionation [Eq. (6-1)].



These bimolecular chain-terminating reactions render radical polymerizations less controllable than their ionic counterparts, where the charged growing ends are repulsive to each other and free from such reactions, although ionic polymerizations often suffer from other side reactions, such as chain-transfer and unimolecular termination reactions. Indeed, about 40 years ago, Szwarc and his associates discovered the living anionic polymerization of styrene with sodium naphthalenide in which chain transfer, termination, and other side reac-

tions are virtually absent (Szwarc, 1956). In this case, the realization of a living process is due to the inherent stability of the carbanionic species per se, which does not lead to undesirable reactions and stays alive for a long time if only under such stringent conditions as anhydrous, oxygen free, and low temperature. The last decade, in particular, has witnessed further progress in the precision control of chain polymerizations via anionic, cationic, metathesis, and coordination mechanisms (Webster, 1991; Aida, 1994; Hirao and Nakahama, 1994; Sawamoto, 1993; Kennedy, 1995; Hsieh and Quirk, 1996; Matyjaszewski and Sawamoto, 1996; Breslow, 1993).

Despite the inherent undesirable reactions, radical polymerizations have been widely used in both industrial and laboratory scale processes, because they have advantages that readily override the disadvantage, i.e., the radical intermediates are highly tolerant to impurities like water and polar hydroxy or amino functional groups. This makes it possible to conduct radical reactions under mild conditions (e.g., in water) and without stringent purification of chemicals and protection of the functional groups. However, radical polymerization has rarely been used for the precision synthesis of polymers with well-controlled structures.

### 6.1.2 Living or Controlled Radical Polymerization: General Principles

Such a pessimistic view of uncontrollable radical reactions has been changing in both polymer and small molecule synthesis, as described in recent reviews. In organic synthesis, on the one hand, numerous radical reactions are now both chemo- and regioselective (Curran et al., 1996). Even stereoselectivity can be achieved with an understanding of the structure of the radical inter-

mediate. In polymer chemistry, on the other hand, radical polymerizations have become increasingly controllable with the use of judiciously designed initiating systems (Georges et al., 1994a; Davis et al., 1995a; Hawker, 1996; Sawamoto and Kamigaito, 1996a; Davis and Haddleton, 1995). It is not accidental but surprising that the key to controlling both radical addition reactions and radical polymerizations appears to be common, namely, to lower the concentrations of transient radical species (Curran et al., 1996; Matyjaszewski and Sawamoto, 1996). This can minimize the rate of reaction between the radical species themselves, suppress the unfavorable reactions, and thereby promote favorable selective reactions between the radical intermediate and a substrate molecule or monomer. Such conditions can be accomplished by a judicious choice of the radical resources, reaction partners, temperature, and other variables.

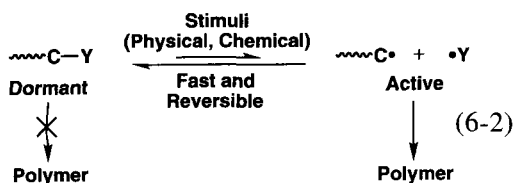
The recently developed living radical polymerizations, in general, adopt a similar strategy to decrease the concentration of the radical intermediate, i.e., the growing reactive radical species is reversibly converted into the dormant species with a covalent bond such as C–S, C–ON, C–halogen, C–Co, etc. [Eq. (6-2)] (Sawamoto and Kamigaito, 1996a). The growing carbon-centered radical therein is rapidly and reversibly capped with its counterpart, mostly a heteroatom-centered radical, to be converted into the covalent bond (or dormant species) which can be easily and homolytically cleaved again into the growing radical species by physical (thermal or photochem-

ical) or chemical (catalytic) stimulus. The existence of such a rapid and reversible interchange equilibrium between dormant and active growing species is crucial in the precision control of radical polymerizations from at least the following two viewpoints. First, it lowers the concentrations of the growing radical species and thereby suppresses their bimolecular termination reactions [see Eq. (6-1)]. Second, its reversibility and fast exchange give an almost equal opportunity of propagation to each growing polymer, which results in the formation of polymers with nearly uniform molecular weights or narrow molecular weight distributions (MWDs).

Thus, to effect such a dynamic, homolytic equilibrium for radical propagation, an effective capping reagent that fulfills the following criteria should be selected. The capping reagent should effectively react with the propagating carbon-centered radical to suppress its concentration. The resultant covalent bond, in turn, can be cleaved homolytically and rapidly to regenerate the growing radical species and the capping moiety. The equilibrium is shifted to the dormant covalent species. The capping reaction should proceed at least as fast or faster than the propagation. The capping reagent should preferentially react with the carbon-centered radical and not the monomer.

In parallel with the selection of the capping reagent, the design of an effective initiator which can induce rapid and quantitative initiation is important for controlled polymerizations. Most typically, such an initiator mimics the dormant polymer terminal, e.g.,  $(\text{CH}_3)_2\text{CBr}(\text{CO}_2\text{CH}_3)$  for methyl methacrylate, where the bromine is the capping moiety. This ensures that initiation proceeds at almost the same rate as the propagation.

Briefly speaking, the controlled radical polymerization stems from the introduction



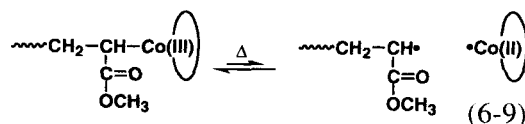
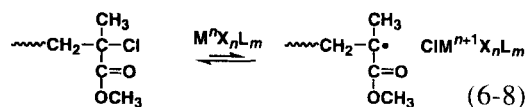
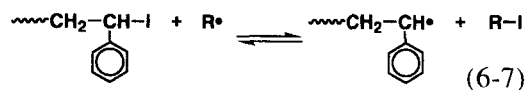
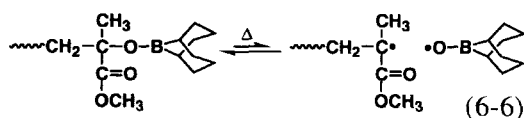
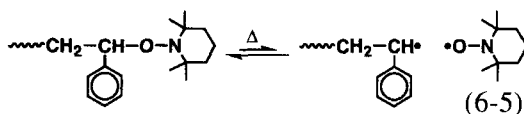
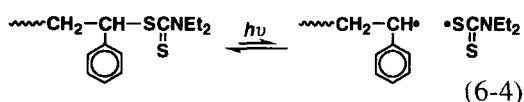
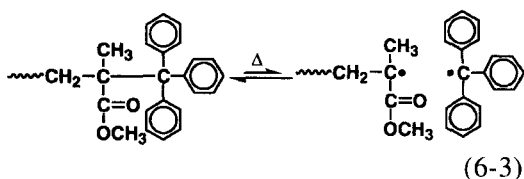
of the dormant species with a potentially active covalent bond into polymer terminals as well as initiators, which warrants suppression of the undesirable radical–radical reactions and virtually equal probability of growth for all polymer chains.

This chapter discusses recent developments in living or controlled radical polymerizations in relation to the use of covalent/dormant species; literature coverage is up to around the end of 1996. The following sections are thus organized in terms of the types of covalent bonds utilized for growing radical formation; relatively large portions are devoted to the systems involving C–ON bonds (nitroxides, Sec. 6.2.2.2) and C–halogen bonds (with metal-assisted, Sec. 6.2.3.2), as judged from the current literature trend. In organic chemistry the term “living radical” sometimes means a radical that is stable for such a long period as to be detected by electron spin resonance (ESR). In this chapter, however, we will use the term “living” for any polymerization that can control the molecular weights and the MWDs of the produced polymers. The term “living” is now extensively under discussion, and it is not always easy and straightforward to distinguish truly “living” polymerizations from their “controlled” counterparts.

## 6.2 Living Radical Polymerization Involving Covalent Dormant Species

Because of the current rapid development of living radical polymerization, an increasingly wide variety of covalent bonds have been utilized for dormant species from which actual growing radicals form [Eq. (6-2)]. For simplicity in this chapter, these covalent bonds are classified into four large

groups (1) C–C, (2) C–O and C–S, (3) C–halogen, and (4) C–metal [Eqs. (6-3) to (6-9)]. On the basis of this classification, various living (or controlled) radical polymerization systems are discussed, where the covalent bonds are activated into radical species thermally, photochemically, or by transition metal complexes. The degree of controllability and the kind of applicable monomer depend on both the bonds and the stimuli employed. Detailed information was added where necessary.



### 6.2.1 Carbon–Carbon Bonds

Free radical chemistry dates back to 1900 when Gomberg discovered that the triphenylmethyl radical ( $\text{Ph}_3\text{C}\cdot$ ) exists in equilibrium with its dimer. This radical is stable in oxygen-free benzene due to the delocalization of an unpaired electron on the three phenyl rings as well as steric hindrance around the carbon radical center. Such stable carbon-centered radicals can form covalent but labile C–C bonds with radical growing polymer terminals, where the bonds can be cleaved thermally and reversibly to generate the stable radicals and the radical growing species [Eq. (6-3)].

In fact, phenylazotriphenylmethane (**1**) (Fig. 6-1), induced the controlled radical polymerization of methyl methacrylate (MMA), where the phenyl radical from **1** adds to the monomer to initiate the polymerization, whereas the triphenylmethyl radical reversibly forms a covalent bond with the growing end (Otsu et al., 1982). A series of compounds with multi-aryl substituents (**2–6**) (Fig. 6-1) have also been employed as “iniferters” for thermal polymerizations of methyl methacrylate (MMA) and styrene at 60–90°C (Otsu et al., 1982, 1987; Bledzki and Braun, 1983; Otsu and Tazaki, 1986). The term “iniferter” was given by Otsu and Yoshida for compounds that act as *initiator*,

*transfer agent*, and *terminator* [see Eq. (6-10)] (Otsu and Yoshida, 1982). The yield and the molecular weight obtained with these aryl-substituted iniferters increased with time, but the MWDs were rather broad ( $\bar{M}_w/\bar{M}_n=1.5-5$ ). The broadening may be due to the irreversible termination between the polymer terminal and the phenyl ring of the counter radicals, as well as slow inter-conversion between the activated and the dormant species. Recently, it has been reported that  $\text{Ph}_2\text{C}(\text{OH})$ - and related diaryl groups introduced onto polyethylene films led to graft polymerization of methacrylic acid (MAA) and an increase of poly(MAA) yield with time (Yang and Rånby, 1996).

### 6.2.2 Carbon–Oxygen and Carbon–Sulfur Bonds

Carbon–chalcogen (oxygen, sulfur, and selenium) bonds can undergo photochemical or thermal homolysis to generate a pair of carbon- and chalcogen-centered radicals. Some of such group 6 heteroatom-centered radicals are stabilized by the resonance effects of the substituents and are effective in the control of radical polymerizations. In fact, there are a number of examples of the use of C–S and C–O bonds for living/controlled radical polymerizations [Eqs. (6-4)

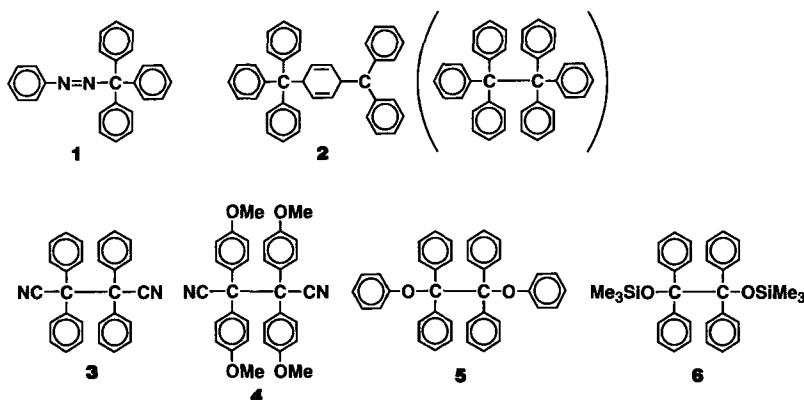
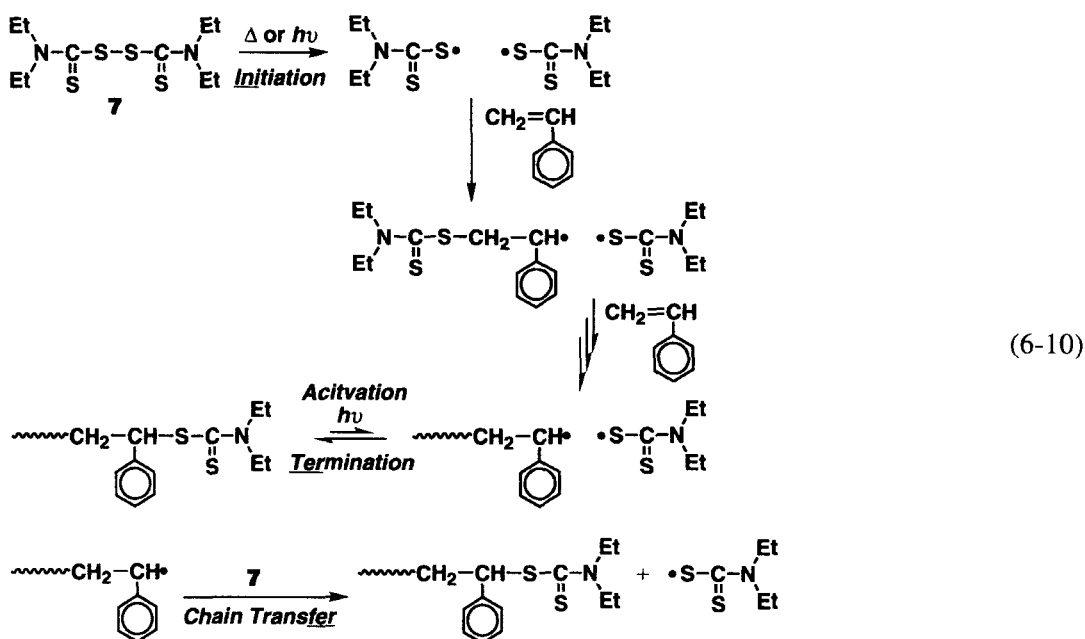


Figure 6-1.





to (6-6)]. Among them, the nitroxide-mediated living radical polymerization is now one of the most extensively studied systems in this field (Georges et al., 1994a; Hawker, 1996).

### 6.2.2.1 Carbon–Sulfur Bonds

Living radical polymerization based on C–S bond activation was first reported by Otsu and Yoshida in 1982. A series of sulfur compounds has been employed as iniferters for living radical polymerizations of styrene and MMA (Otsu and Yoshida, 1982; Kuriyama and Otsu, 1984; Otsu et al., 1989; Endo et al., 1992; Doi et al., 1994a, b; Turner and Blevins, 1990; Lambrinos et al., 1990). For example, tetraethyldithiuram disulfide (**7**) induces the living radical polymerization of styrene under UV irradiation at 30°C [Eq. (6-10)] (Otsu and Yoshida, 1982). Photochemical or thermal cleavage of the S–S bond of **7** generates two identical sulfur-centered radicals, one of which subsequently adds onto the monomer. The

other radical acts as a terminator that can reversibly form the dormant C–S bond with the propagating radicals. Such a C–S bond is also generated by chain-transfer reaction with **7**. Thus **7** acts as an iniferters and results in the C–S bond which is activated photochemically.

A problem with the use of such a symmetrical sulfur compound is that propagation may take place at both the  $\alpha$ - and  $\omega$ -ends of the C–SC(S) bonds, although the primary carbon radical at the  $\alpha$ -end seems more difficult to form than the secondary benzylic at the  $\omega$ -end. Recently, spin-trapping experiments with model compounds for both  $\alpha$ - and  $\omega$ -terminals suggested that the C–SC(S) bond at the polystyryl  $\alpha$ -ends does not cleave (Doi et al., 1994). However, such a problem is fully avoidable with the use of benzylic dithiocarbamates like **12** (Fig. 6-2), because the polymerization is initiated by a more reactive alkyl radical generated by the photochemical cleavage of the C–S bond, whereas the propagating chain end is capped with a less reactive sulfur-cen-

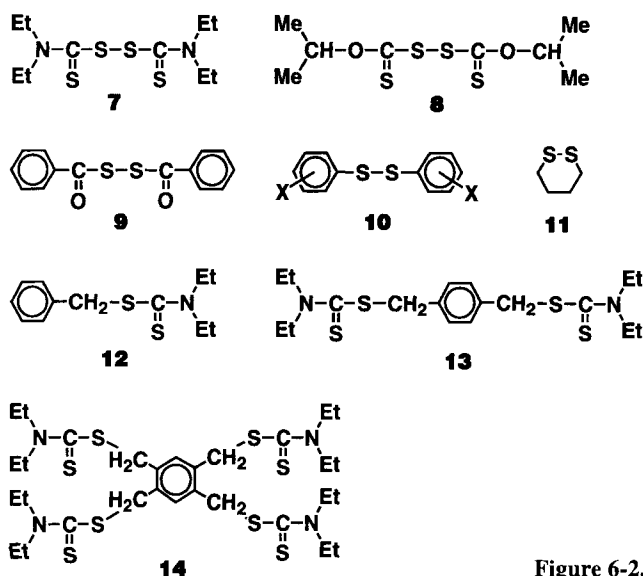


Figure 6-2.

tered radical (Otsu et al., 1982). In this case, a low temperature is favorable for better-controlled polymerizations to minimize initiation from the sulfur-centered radical.

Control of acrylates polymerizations had been difficult by sulfur iniferters (Turner and Blevins, 1990; Lambrinos et al., 1990), but has recently been achieved by two-component initiating systems consisting of **12** and **7**. The latter serves as an efficient donor of the sulfur-centered radical which prevents irreversible bimolecular termination between the growing polymer radicals, whereas **12** serves as an initiator (Doi et al., 1994b). Initiation preferentially occurs from **12**, because **7** is less reactive for acrylate polymerizations. Telechelic and star polymers are prepared with benzylic multifunctional iniferters (**13** and **14**) (Kuriyama and Otsu, 1984).

In general, sulfur-based living radical polymerizations lead to an increase of molecular weight with time and conversion, while the MWDs are relatively broad ( $M_w/M_n \geq 1.5$ ) and the reactions are slow and sometimes unquantitative. Another prob-

lem is the possible generation of new polymer chains via addition of the sulfur-centered radicals to the monomers, although the reactivity of the sulfur radicals is smaller than that of the carbon-centered growing radicals. These defects should be overcome for better-controlled polymerizations.

#### 6.2.2.2 C–ON Bonds

##### *Discovery and Mechanistic Aspects of Nitroxide-Mediated Living Polymerization*

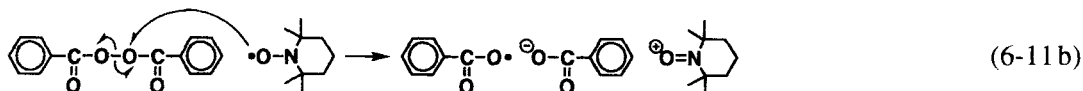
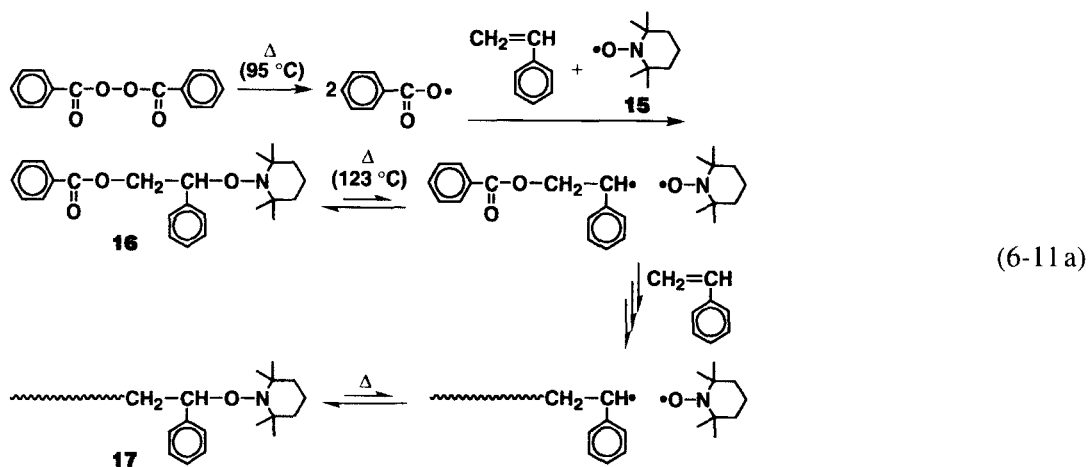
Nitroxides such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, **15**) are stable radical species. They do not react with oxygen-centered radicals but form C–ON bonds with carbon-centered radicals. The latter process is reversible where the C–ON bonds can be cleaved thermally to regenerate the carbon-centered and the nitroxide radicals. The use of C–ON bonds for controlled radical polymerizations was reported by Rizzardo and Solomon about 10 years ago for acrylate monomers (Salomon et al., 1986). Subsequently a similar strategy was

more extensively employed for styrene by Georges et al. (1993), who used TEMPO in conjunction with benzoyl peroxide (BPO) [Eq. (6-11 a)]. This marks the beginning of recent developments in this field, because the degree of molecular weight control is much superior to that of all the former systems.

For example, polymerization was initiated by preheating a mixture of styrene, BPO, and TEMPO at 95 °C for 3.5 h, where benzoyloxy radicals from BPO added to the monomer, and subsequent heating to 123 °C for 69 h in bulk gave polymers with a narrow MWD ( $\bar{M}_w/\bar{M}_n = 1.27$ ) and  $\bar{M}_w$  of 10000 (Veregin et al., 1993). This temperature program uses the fact that BPO decomposes at 95 °C whereas the styrene–TEMPO linkage does not. This linkage dissociates above 135 °C. Throughout the nearly quantitative polymerization, the polymer MWDs are fairly narrow and  $\bar{M}_n$  increases in proportion to monomer conversion. BPO can be replaced with azobisisobutyronitrile (AIBN), but the polymer MWDs are apparently broader than those with BPO (Odell et al., 1995; Hawker et al., 1996b).

As shown in Eq. (6-11 a), the living polymerization is initiated by the decomposition of BPO, the formation of the adduct (**16**) of BPO, styrene, and TEMPO, and thermal activation of the C–ON bond therein. ESR studies have shown that the added TEMPO reversibly forms C–ON bonds with the growing radical terminals. Another role of TEMPO is to induce the decomposition of BPO [Eq. (6-11 b)], the activation energy of which is  $40 \pm 5$  kJ/mol, lower than for the thermal decomposition of BPO (125 kJ/mol).

The adduct **16** seems to be a real initiator, and in fact has been employed as an initiator for the living radical polymerization of styrene at 130 °C (see the next section) (Veregin et al., 1995; Hawker, 1994). The obtained polymers had narrow MWDs ( $\bar{M}_w/\bar{M}_n = 1.1 - 1.4$ ) and controlled molecular weights up to  $\bar{M}_n = 100000$ , which agreed well with the calculated values assuming that one molecule of **16** generates one living polymer chain. According to a recent paper, such a one-component initiating system is superior to the original BPO/TEMPO two-component counterpart in terms of the control in high molecular



weight regions (Hawker et al., 1996b). Some papers on this and similar two-component systems also suggest that the molecular weights depend on the concentration of nitroxide radicals as well (Veregin et al., 1996a; Yoshida and Okada, 1996; Puts and Sogah, 1996), which cannot be explained simply by the mechanism shown in Eq. (6-11a). Despite some complexities, however, these results suggest that the nitroxide-mediated polymerizations proceed via the thermal activation of the C–ON bonds at polystyrene terminals.

Extensive kinetic and ESR analyses have been done for elucidating the mechanism of the nitroxide-mediated living polymerization. When the polymerization is initiated by the mixture of BPO and TEMPO, a slight excess of TEMPO is necessary over BPO (usually TEMPO/BPO = 1.1–1.3 mole ratio) (Veregin et al., 1996a). The polymerization rate was inversely proportional to the TEMPO concentration. This suggests the existence of equilibrium between the growing end and TEMPO. Therein the forward process, the dissociation of TEMPO, is more favored from a polymeric chain end than from a unimer (**16**); the activation energy was 82 as opposed to 130 kJ/mol (Veregin et al., 1996a). In the backward process, the trapping rate of the growing polymer radical by TEMPO ( $k_L = 1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) is over 3 orders of magnitude slower than a diffusion-controlled reaction but as fast as polystyrene radical–radical termination and other nitroxide-trapping reactions in organic chemistry (Veregin et al., 1996b). However, the excess nitroxide is to permit a faster exchange reaction between the dormant and the growing species. Similar values of these rate constants have also been obtained by a computer simulation, where  $k_L = 8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  and  $K = 10^{-11} \text{ M}^{-1}$  (Greszta and Matyjaszewski, 1996b). The nitroxide-mediated living polymerization is free

from the gel effects which are observed in usual radical polymerizations (Saban et al., 1995). This may afford significant benefits to industrial scale bulk polymerizations.

The nitroxide-mediated radical polymerization is believed to occur via the radical species generated from the homolytic and reversible dissociation of the terminal C–ON bond [Eq. (6-11a)]. Although this mechanism implies that the polymerization rate is proportional to the C–ON concentration, it has recently been revealed that the rate does not depend on it (Catala et al., 1995; Hammouch and Catala, 1996). One possible explanation would be aggregation of the dormant polymers, but the most plausible explanation has been provided by kinetic and ESR analyses of the polymerizations mediated by the adduct of polystyrene and TEMPO (PS–TEMPO, **17**) (Fukuda and Terauchi, 1996; Fukuda et al., 1996b). First, the polymerization rate with PS–TEMPO turned out to be equal to one without it, i.e., the rate of thermal polymerization. Even in controlled-radical polymerizations, irreversible termination between the polymer terminals occurs, and thermal initiations are necessary for a constant supply of initiating radicals to compensate for the loss of growing radicals. The role of the nitroxide adduct is therefore to afford almost the same opportunity of growth to all the polymer terminals via the fast equilibrium between the dormant C–ON species and the growing radical species. Also, the total number of thermally initiated polymer terminals is much smaller than the number of PS–TEMPO polymers. Thus the molecular weights were controlled by the ratio of the concentration of monomer to the TEMPO adduct, and the MWDs stayed narrow because of the rapid interconversion between the dormant and the active growing ends.

Similar conclusions have been derived by other research groups (Greszta and Matyjas-

zewski, 1996; Hammouch and Catala, 1996b). The polymerization rates can be increased by the addition of conventional radical initiators like 1,1'-azobis(2-cyclohexanecarbonitrile) without affecting molecular weights up to about 40% conversion (Hammouch and Catala, 1996b). Irreversible decomposition of the adducts and the contribution of thermal initiation have also been suggested (Li et al., 1995; Greszta and Matyjaszewski, 1996a).

Living polymerizations with nitroxides are usually performed in bulk. The effects of solvents like chlorobenzene were studied, and larger amounts of solvent sometimes led to bimodal MWDs of product polymer (Hawker et al., 1996b). This may be due to the occurrence of thermally initiated autopolymerization of styrene for longer reaction times. These results mean that the irreversible side reactions are not entirely suppressed in the nitroxide-mediated polymerizations, and control of the molecular weights and MWDs is simply ascribed to the existence of compounds that can reversibly form the covalent species so as to give the same growth chance to all the polymer terminals. This is in contrast to recognition of the nitroxide-mediated living radical polymerizations where irreversible termination is suppressed by the reversible formation of stable C–ON bonds. Such mechanistic studies are now being carried out extensively and we hope that conclusions will be reached shortly.

### *Design of Initiating Systems*

Despite some mechanistic controversies, as summarized above, progress has been made in devising new initiating systems for the nitroxide-based living processes. These systems can be divided into two groups in terms of the number of components of the initiating systems: mixtures of a conven-

tional radical initiator and a stable nitroxide radical (e.g., BPO and TEMPO) and one-component initiators with pre-formed C–ON bonds. For both groups, the choice of the nitroxide moiety is important for controlled polymerization to occur. For the one-component initiating systems, choice of the carbon-centered radical species to be generated via the dissociation of the C–ON bonds is important as well.

In addition to TEMPO (**15**), related nitroxide compounds (**18–23**) (Fig. 6-3) have also been effective in controlled radical polymerizations of styrenes. Compounds **18–20** induced faster living polymerizations of styrene than TEMPO (Kazmaier et al., 1995; Veregin et al., 1995; Catala et al., 1995; Puts and Sogah, 1996). Effects of the nitroxide substituents on the polymerizations have been investigated independently by two groups, based on the semiempirical molecular orbital calculations of the model compounds with a C–ON bond (Moad and Rizzardo, 1995; Kazmaier et al., 1995; Veregin et al., 1995). The principal conclusion of these studies is that the polymerizations proceed faster using a C–ON bond with less bond dissociation enthalpy. For example, the polymerization with **19** proceeded about three times faster than with TEMPO, where the bond dissociation enthalpy of the former is smaller (92 versus 109 kJ/mol). The bond dissociation enthalpy may also affect the controllability of the molecular weights and MWDs. The bond dissociation enthalpy of C–SC(S)NR<sub>2</sub>, which has been employed for living radical polymerizations but is less controllable than TEMPO, is much larger than for the C–TEMPO bond (163 versus 109 kJ/mol). This means that a weaker bond is suited to controlled radical polymerizations based on such homolytic cleavage. The nitroxyl radical with phosphoric acid, **23**, accelerates the polymerization probably due to the induced dissociation of the C–ON

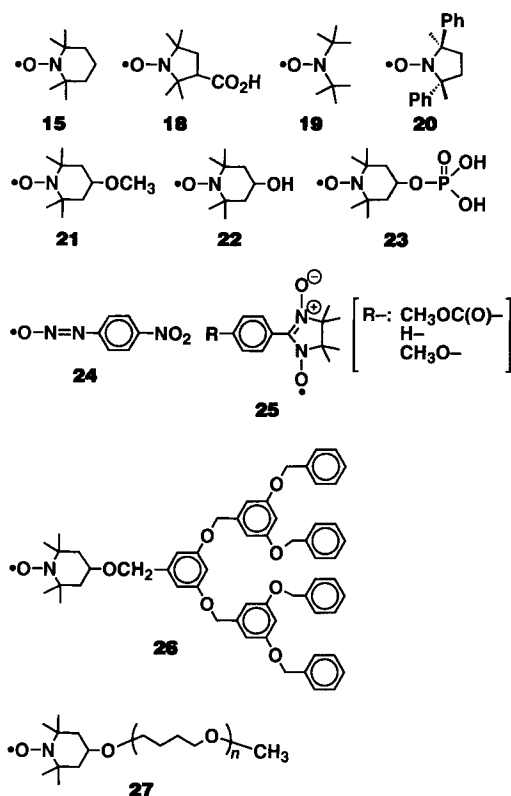


Figure 6-3.

bond via intramolecular interaction with the phosphoric acid function (Matyjaszewski et al., 1995a).

A similar oxygen-centered radical, **24**, can be generated from the one-electron oxidation of arene diazonium ions and has been used for acrylate polymerizations (Dru-liner, 1991). Its controllability is inferior to that of the usual nitroxides, which can also be predicted from the larger dissociation energy of the C–ON bond (142 kJ/mol) derived from **24** on the basis of semiempirical calculation (Kazmaier et al., 1995). The use of **25** permitted the study of the electronic effects of the nitroxide radicals, although the polymerizations were less controlled than the others (Shigemoto and Matyjaszewski, 1996). On increasing the electron density of R groups of **25**, the MWDs of the

produced polystyrene became narrower, whereas the bond became more easily decomposed. The stereocontrol has been also examined by the use of a chiral nitroxide, **20** (Puts and Sogah, 1996). The polystyrenes obtained with the chiral nitroxide had the same tacticity as those with achiral compounds. This suggested that the polymerization proceeds predominantly from the state where the nitroxide dissociates completely from the growing polymer terminal. The physical effect on the suppression of the irreversible terminations imposed by the steric hindrance is expected in the system with a dendrimer nitroxide like **26** (Matyjaszewski et al., 1996). Contrary to what was expected, the molecular weights and MWDs were less controlled. The nitroxide radical with a polymer chain (**27**) can be employed for the synthesis of block copolymers as described below (Yoshida and Sugita, 1996).

For the one-component initiators, a series of compounds that have nitroxide moiety and aryl groups in the counterpart moiety have been synthesized via various methods and employed for polymerizations of styrenes (Kazmaier et al., 1995; Hawker, 1994; Hawker et al., 1996b; Catala et al., 1995; Connolly et al., 1996; Howell et al., 1996). Mostly, they are nitroxide-capped phenylethyl compounds. It has been revealed that an  $\alpha$ -methyl group is essential for radical polymerizations where the molecular weights are controlled by the feed ratio of the initiator to the monomer, and the MWDs were as narrow as  $\bar{M}_w/\bar{M}_n \sim 1.2$  (Fig. 6-4). As far as the  $\alpha$ -methyl group exists in the initiator, a variety of substituents can be introduced on the aryl groups or the  $\beta$ -carbon atom without seriously affecting the molecular weights and MWDs of the produced polymers.

One of the problems of nitroxide-mediated living radical polymerizations is the slow rate of the polymerizations. For example, in

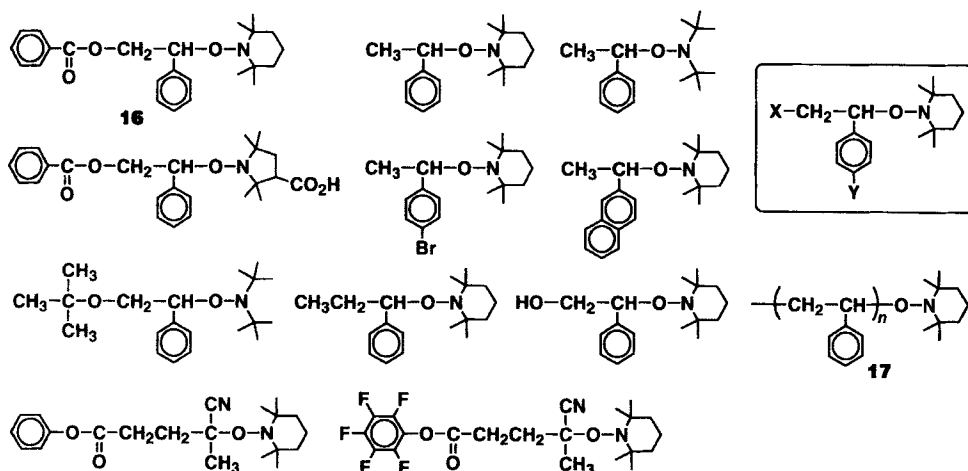
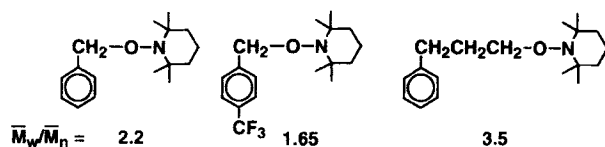
**Efficient Initiators**  $\bar{M}_w/\bar{M}_n = 1.1-1.2$ **Less Efficient Initiators**

Figure 6-4.

bulk polymerizations of styrene at 130 °C, over 50 h are needed for over 90% conversion of the monomer in both the one and two-component initiating systems (Hawker et al., 1996b). To improve the slow reactions, some protonic acids have been added (Georges et al., 1994b, 1995; Odell et al., 1995; Veregin et al., 1996c; Li et al., 1995; Baldoví et al., 1996; Puts and Sogah, 1996; Howell et al., 1996). The acceleration effects of camphorsulfonic acid [28, CSA (Fig. 6-5)] were first observed in the BPO/TEMPO-mediated systems (Georges et al., 1994b). For example, conversion reached 92% in 5.5 h at 130 °C in the presence of 0.027 M CSA, while the conversion

was only 24% in its absence under otherwise the same conditions. Larger acceleration effects were observed with the use of 2-fluoro-1-methylpyridinium *p*-toluenesulfonate (29, FMPTS) (Odell et al., 1995). However, such rate increase was not observed with benzoic acid 30 and diphenylacetic acid 31. Originally, the addition of CSA was intended to suppress thermal initiation, but such effects were not actually observed in the presence of TEMPO (Georges et al., 1995). The acceleration can be explained in two ways, either by a decrease in the free TEMPO concentration (Veregin et al., 1996c) or a decrease in the trapping reaction rate of the growing poly-

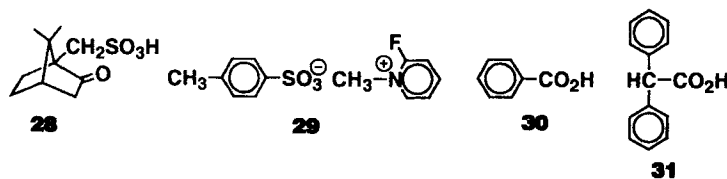


Figure 6-5.

mer terminal by TEMPO via a kind of solvation effect by CSA (Baldoví et al., 1996). At present, the roles of such acids seem unclear because FMPTS does not affect the TEMPO concentration (Odell et al., 1995) and some systems with other nitroxides like **20** are free from such acceleration effects of CSA (Puts and Sogah, 1996). More comprehensive explanations are awaited.

### Monomers and Block or Random Copolymers

The nitroxide-mediated living polymerizations can be applied not only for styrene but also for its derivatives bearing functional groups on the phenyl ring (Keoshkerian et al., 1995; Hawker, 1994; Hawker et al., 1996a; Yoshida, 1996; Bertin and Boutevin, 1996). For example, the BPO/TEMPO systems induced controlled polymerizations of *p*-chloromethylstyrene [**32** (Fig. 6-6)] to give polymers with controlled molecular weights ( $\bar{M}_n=12000$ ) and relatively narrow MWDs ( $\bar{M}_w/\bar{M}_n\sim 1.5$ ) (Bertin and Boutevin, 1996). Similar control cannot be attained in anionic polymerization because of the side reactions between the ionic growing terminal and the functional groups in the monomers. Well-defined block and random copolymers with styrene and **32** (Hawker et al., 1996; Bertin and Boutevin, 1996), **33** (Hawker 1994), or **34** (Yoshida, 1996) have also been synthesized by the nitroxide-based living radical systems. Among these, of particular interest is the living polymerization of the styrenesulfonic acid sodium salt (**35**) initiated with potassium persulfate

( $K_2S_2O_8$ ) as the radical initiator in the presence of TEMPO in aqueous ethylene glycol (80%) at 125 °C (Keoshkerian et al., 1995). Increases in conversion and molecular weight with time have been observed, and the MWDs were narrow throughout the reactions ( $\bar{M}_w/\bar{M}_n=1.1-1.3$ ). Such aqueous living polymerizations have not been accessible by anionic mechanisms either.

There have been several efforts to control radical polymerizations of acrylic monomers with nitroxides, which were in fact first employed for methyl acrylate (MA), ethyl acrylate (EA), etc. (Solomon et al., 1986). For example, the polymerization of MA in bulk at 100 °C gives polymers with  $\bar{M}_n=2500$  and  $\bar{M}_w/\bar{M}_n=1.7$ . Block and random copolymerizations between MA and EA are also possible, affording copolymers of similar MWDs. Under the required conditions, the polymerization of MMA is less controllable with an oxygen-centered radical (**24**) (Dru-liner, 1991) or with TEMPO in the presence of CSA (Steenbock et al., 1996). This is partly due to  $\beta$ -H abstraction from the terminal methyl group of poly(MMA) by the nitroxide moiety (Solomon et al., 1986).

In contrast, the nitroxide-based systems are effective in controlled random copolymerizations between styrene and such monomers as acrylonitrile (AN), MA, EA, MMA, vinyl carbazole, and butadiene (Georges et al., 1993; Hawker et al., 1996a; Fukuda et al., 1996). The MWDs of the copolymers were narrow ( $\bar{M}_w/\bar{M}_n\sim 1.2$ ) when the molar composition of styrene was above 0.8; with decreasing the styrene content, the molecular weights became lower than the

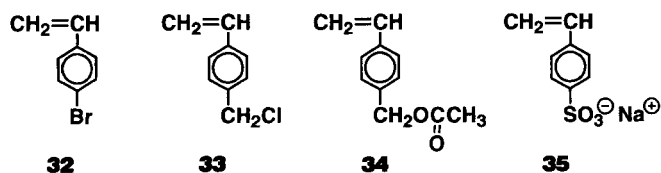


Figure 6-6.



calculated values, and the MWDs became broader (Hawker et al., 1996). The latter deviation may be attributed to the lower stability of the C–ON bonds at the acrylic polymer terminals (Solomon et al., 1986), or to the difficulty of effective thermal initiation from the acrylic monomers (see above) (Fukuda and Terauchi, 1996). The sequence distribution and tacticity of the random copolymers were the same as those obtained in conventional radical polymerizations (Hawker et al., 1996a; Fukuda et al., 1996b). The TEMPO-based systems also led to living donor–acceptor copolymerization between styrene and *N*-cyclohexylmaleimide which is faster than the corresponding homopolymerization of styrene (Schmidt-Naake and Butz, 1996). Block copolymers consisting of polystyrene and random copolymers such as poly(styrene-*co*-AN) or poly(styrene-*co*-*N*-cyclohexylmaleimide) can be prepared (Fukuda et al., 1996a; Schmidt-Naake and Butz, 1996).

The synthesis of block copolymers containing homosegments of acrylic monomers is difficult, as anticipated from the unsatisfactory results on the homopolymerization of acrylic monomers with the nitroxide-based systems. The sequential addition of MMA or EA into living polystyrene prepared by AIBN/TEMPO gave mixtures of the block copolymers and homopolymers (Steenbock et al., 1996). Another method for the synthesis of block copolymers is a combination of a nitroxide-mediated radical living polymerization with the anionic or cationic counterparts. For instance, the nitroxide-terminated polystyrene (**17**) prepared by anionic living methods has been employed as a macroinitiator for a subsequent nitroxide-mediated radical polymerization of acrylates (Yoshida et al., 1994). In contrast to the sequential living radical polymerization, a high blocking efficiency (96%) was obtained. A poly(THF)-substi-

tuted nitroxide (**27**) obtained by cationic living methods can be employed as a nitroxyl radical for living polymerizations of styrene to afford poly(THF)-*block*-polystyrene, although the two segments are connected with a weak C–ON bond (Yoshida and Sugita, 1996).

### Synthesis of Well-Defined Polymers

Unimolecular initiating systems permit the synthesis of polymers with well-controlled structures like end-functionalized, multi-armed, hyper-branched, and graft polymers, in addition to the block copolymers discussed above.

Hydroxy- and amino-terminated polystyrenes have been obtained via the living polymerization of styrene with functionalized TEMPO adducts, **36** and **37** (Fig. 6-7), respectively (Hawker and Hedrick, 1995; Frank et al., 1996). Both end-functionalized polymers had narrow MWDs ( $\bar{M}_w/\bar{M}_n = 1.1–1.2$ ) and one initiator moiety at the  $\alpha$ -end, as confirmed by  $^1\text{H}$  NMR and titration of the functional groups. The merit of the use of nitroxide-mediated radical polymerizations for end-functionalization is that protection of functional groups like OH groups is unnecessary, because the dormant terminal as well as the radical growing terminal is robust for such polar functions. The end-functionalized polymers with fluorescent labels can be obtained with **38**.

Bifunctional (**39** and **40**) (Hammouch and Catala, 1996a; Connolly et al., 1996) and trifunctional (**41**) (Hawker, 1995) initiators with TEMPO groups have been employed for controlled radical polymerizations of styrene. For example, **41** generates a three-armed polystyrene with  $\bar{M}_n = 53\,000$  and  $\bar{M}_w/\bar{M}_n = 1.19$  in bulk at  $130^\circ\text{C}$  (Hawker, 1995). Subsequent hydrolysis of the ester linkage at the core part gave polymers of  $\bar{M}_n = 22\,000$  and  $\bar{M}_w/\bar{M}_n = 1.09$ , which

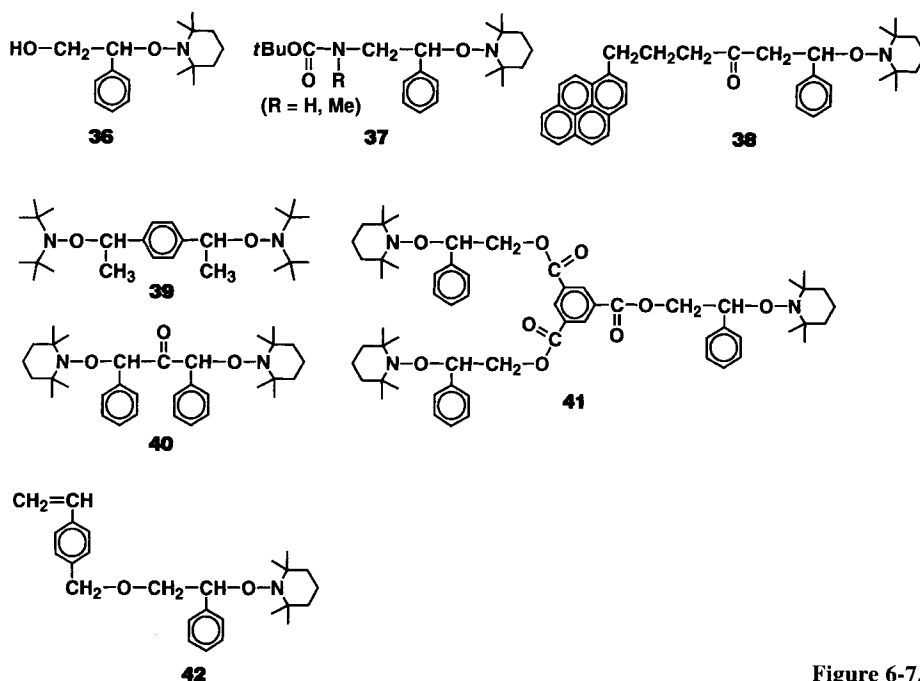


Figure 6-7.

indicates that the arms possess narrow MWDs.

A styrene derivative (**42**) with a pendent nitroxide can be used for the synthesis of graft polymers and hyper-branched polymers. Thus copolymers of styrene and **42** are first prepared by a conventional radical process with AIBN at 65 °C (i.e., below the dissociation temperature of the C–ON bond). By raising the temperature to 130 °C, the nitroxide groups in the side chain are subsequently allowed to initiate the nitroxide-mediated living polymerization of styrene to give graft polymers with arms of nearly uniform molecular weights (Hawker, 1995). Alternatively, the homopolymerization of **42** gave hyperbranched polymers, and the subsequent addition of styrene gave multi-arm star polymers, because the precursors possessed nitroxide-initiating points in the core (Hawker et al., 1995). Copolymerizations of styrene and **42** at 130 °C led to hyperbranched polymers with larger and less constrained cores.

### 6.2.2.3 Other Carbon–Chalcogen Bonds

Carbon–chalcogen bonds other than C–ON are also utilized for controlled polymerizations, although the controllability is generally inferior. For instance, the oxidation adduct of 1-octyl-9-borabicyclononane has also been utilized for MMA polymerization, where the C–OB bond is thermally activated into a carbon-centered radical and the borinate counter-radical [Eq. (6-6)] (Chung et al., 1996). The MWDs of polymers thus formed are broader ( $\bar{M}_w/\bar{M}_n=2.5$ ), but it is interesting that the borinate radical is stabilized by the empty p-orbital of the boron, which is in contrast to the stabilization of nitroxide radicals by the filled p-orbital of the nitrogen.

Recently, selenide compounds like diphenyl diselenide ( $\text{PhSe}-\text{SePh}$ ) and benzyl selenide ( $\text{PhCH}_2-\text{SePh}$ ) have been employed as photoinitiators for controlled radical polymerizations of styrene and MMA

(Kumazawa et al., 1995). The molecular weights increased with conversion, and the MWDs were relatively broader ( $\bar{M}_w/\bar{M}_n = 1.5\text{--}2.0$ ), although the details and the relevance to living polymerization are still to be examined.

### 6.2.3 Carbon–Halogen Bonds

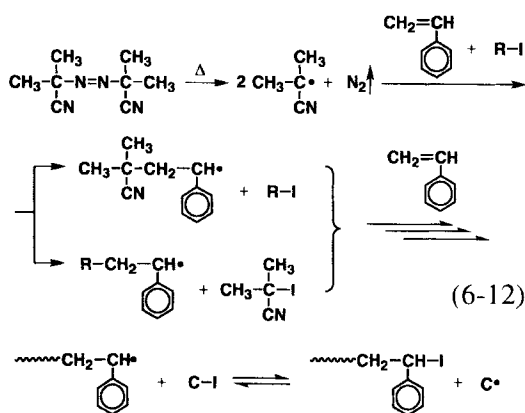
As with the carbon–chalcogen bonds, some carbon–halogen bonds are susceptible to homolytic cleavage. The carbon-centered radicals can be formed by the abstraction of halogen atoms by radical species or by organometallic compounds (e.g., tin derivatives). In organic synthesis, many organic halides have been employed as precursors for radical intermediates to effect selective reactions. Such labile C–X (X=I, Br, Cl) bonds have recently been applied for controlled radical polymerizations as well. This section will treat the living or controlled radical polymerizations where the carbon–halogen bonds are activated by (1) a small amount of carbon-centered radicals [Eq. (6-7)] or by (2) transition-metal complexes [Eq. (6-8)].

#### 6.2.3.1 Carbon–Iodine Bonds for Degenerative Transfer

The dissociation energy of carbon–iodine bonds is relatively low and susceptible to homolytic cleavage in the presence of radical species generated from conventional radical initiators. C–I bond cleavage for controlled polymerizations was first employed in the polymerization of perfluoroalkenes like  $\text{CF}_2=\text{CF}_2$ , initiated with ammonium persulfate in the presence of perfluoroalkyl iodide, e.g.,  $(\text{CF}_3)_2\text{CF-I}$  (Oka and Tatemoto, 1984). The growing radical species is in fast equilibrium with the dormant C–I species, where the latter species is much more abundant than the former. This

permits the molecular weight to be controlled by the feed ratio of the monomer to the iodide compound to give narrow MWDs ( $\bar{M}_w/\bar{M}_n = 1.3$ ).

A similar approach has been adapted for controlled polymerizations of styrene, BA, MA, MMA, and vinyl acetate (VAc) with AIBN or BPO [Eq. (6-12)] (Kato et al., 1994; Matyjaszewski et al., 1995b; Gaynor et al., 1995; N. Ueda et al., 1996). Control of the molecular weights and their distributions was possible for styrene and acrylates, although the MWDs were broader than those for perfluoroalkenes [ $\bar{M}_w/\bar{M}_n \sim 1.5$  (styrene) and 2.0 (acrylates)]. The available iodides include not only perfluoroalkyl iodides but also the hydrogen-iodide adduct of styrene [ $\text{CH}_3\text{CH(Ph)I}$ ] and vinyl ethers [ $\text{CH}_3\text{CH(OR)I}$ ]. Such iodide compounds serve as degenerative transfer agents which can produce C–I bonds reversibly. The mechanism may be similar to that for the nitroxide-mediated living polymerizations where the dormant species is C–ON bonds and the radical species is supplied by thermal initiation. However, the polymerization based on C–I bond activation needs radical resources probably due to the low reactivity C–I bonds. Control of MMA polymerizations was difficult with iodide-based systems. Controlled polymerizations of

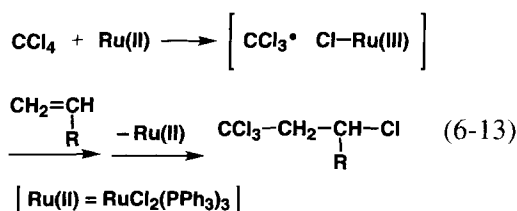


VAc have proved possible recently with the use of a larger amount of AIBN than of the iodide compounds (N. Ueda et al., 1996). The obtained poly(VAc) had a relatively narrow MWD ( $M_w/M_n = 1.3 \sim 1.5$ ), but a still uncontrolled head–head linkage in the main chain structures.

### 6.2.3.2 Carbon–Halogen Bonds Activated with Transition Metal Complexes

Transition metal complexes are now indispensable for the precision synthesis of organic compounds, as well as polymers from almost all perceptible mechanisms including ionic, radical, and coordination (Trost, 1995). The recognition of radical reactions has also changed from uncontrollable to controllable by the emergence of various transition metal complexes that can promote controlled reactions. Owing to their wide range of oxidation states, these complexes generally serve as effective oxidants or reductants to generate radical species from organic precursors. Furthermore, the metal complexes with designed ligands can even permit the stereocontrol of radical reactions.

In metal-catalyzed radical reactions, carbon–halogen bonds can be homolytically cleaved by some transition metals. For example, a ruthenium complex,  $\text{RuCl}_2(\text{PPh}_3)_3$ , homolytically cleaves the C–Cl bonds in  $\text{CCl}_4$  to generate a carbon-centered radical ( $\text{CCl}_3^\bullet$ ), where the ruthenium center is oxidized from divalent to trivalent [Eq. (6-13)] (Matsumoto et al., 1973, 1978; Davis and Groves, 1982). In the presence of an olefin, the trichloromethyl radical adds to the double bond to give a new carbon-centered radical. The radical species subsequently abstracts a chlorine atom from the trivalent ruthenium species to regenerate a C–Cl bond along with a  $\text{CCl}_4$ –olefin adduct and the original divalent ruthenium species. During the addition reaction, therefore, the rutheni-



um center undergoes a reversible redox reaction between the divalent and the trivalent states. Such addition reactions are known as Kharasch, or atom-transfer, addition reactions, and are widely employed for inter- and intramolecular reactions for organic synthesis (Curran, 1991; Curran et al., 1996; Iqbal et al., 1994). The suitable metal centers include not only Ru(II) but also Cu(I) (Asscher and Vafsi, 1961, 1963; Bellus, 1985; Udding et al., 1994; Pirrung et al., 1995; Nagashima et al., 1992, 1993), Ni(II) (Inoue et al., 1978; Grove et al., 1988, 1989), Fe(II) (Hayes et al., 1986, 1988; Lee et al., 1988; Lee and Weinreb, 1990), Mo(0) (Davis and Groves, 1982), etc. The efficiency of the metal-catalyzed reactions depends on the central metal, the ligands on the complex, and the halide precursors. Importantly, such specific, metal-catalyzed addition reactions to regenerate a potentially active carbon–halogen bond in the products are more prominent than the stannanes-induced radical reactions where the C–X bonds in the products are usually reduced into unreactive C–H bonds by hydrogen-atom transfer.

Recent developments on transition metal mediated radical reactions in organic synthesis again stimulate polymer chemists to use transition metals for radical polymerizations, although their use for radical polymerizations dates back 20–30 years when transition metal complexes like  $\text{Pt}(\text{PPh}_3)_4$  (Bamford et al., 1968),  $\text{Ni}[\text{P}(\text{OPh})_3]_4$  (Bamford and Sakamoto, 1974a),  $\text{Mo}(\text{CO})_6$  (Bamford and Sakamoto, 1974b), and  $\text{RhCl}$

(CO)(PPh<sub>3</sub>)<sub>2</sub> (Kameda and Itagaki, 1973) were employed in conjunction with CCl<sub>4</sub> or the related polyhalogeno compounds as redox initiators. In these now classical systems, the initiation involves a similar redox reaction via homolytic cleavage of a carbon–halogen bond, but propagation proceeds by the conventional, poorly controlled radical mechanism, which may be due to the irreversible formation of the radical species from such metal complexes. Polymerization with reduced nickel [Ni(0)] in conjunction with benzyl halides was also reported, where the molecular weights increased with conversion, while the MWDs were bimodal (Otsu et al., 1990).

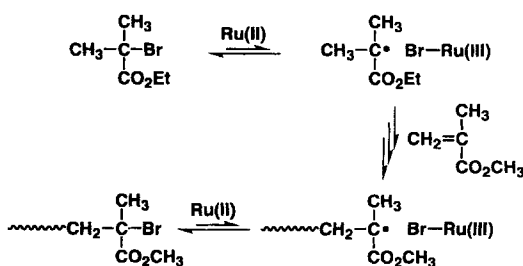
However, recent uses of transition metal complexes like RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> and CuCl (complexed with bipyridine ligands) enable living or controlled radical polymerizations of methacrylates, acrylates, and styrenes, opening a new vista in radical polymerization. The recent developments in transition-metal catalyzed radical polymerizations are comparable to those in the nitroxide-mediated counterparts in terms of degree of control, and have given the variety and versatility of transition metal complexes; these processes might be applicable to a wider range of vinyl monomers or under varying reaction conditions. The following section will deal with the developments in such transition-metal catalyzed radical polymerizations. It is important to note here that these systems employ “chemical stimuli” to generate radical intermediates, whereas those with TEMPO and related nitroxides employ “physical stimuli”, mostly thermal.

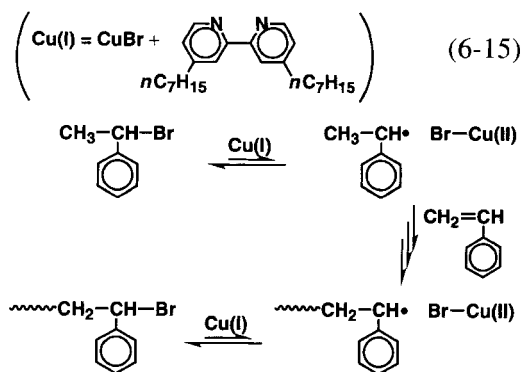
#### *Discovery and Mechanistic Aspects of Transition Metal Mediated Living Polymerization*

The first living radical polymerization based on the activation of C–X bonds with

transition metal complexes was for MMA with CCl<sub>4</sub>/RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> in toluene at 60°C (Kato et al., 1995). The polymerization was initiated by the ruthenium-catalyzed formation of CCl<sub>3</sub>· followed by its addition to MMA and formation of the adduct with a C–Cl bond. Subsequently, the C–Cl bond is reversibly and homolytically activated by the ruthenium complex in the presence of aluminum compounds like MeAl(ODBP)<sub>2</sub> (ODBP=2,6-di-*tert*-butylphenoxy) to induce repetitive similar additions of the carbon-centered radical to MMA. The molecular weights can be controlled by the feed ratio of MMA to CCl<sub>4</sub> (initiator), and the MWDs were fairly narrow ( $\bar{M}_w/\bar{M}_n \sim 1.3$ ). Narrower MWDs ( $\bar{M}_w/\bar{M}_n \sim 1.1$ ) are affordable when the ruthenium catalyst is coupled with CHCl<sub>2</sub>COPh, (CH<sub>3</sub>)<sub>2</sub>C(CO<sub>2</sub>Et)Br, or CCl<sub>3</sub>CO<sub>2</sub>Me as an initiator and Al(OiPr)<sub>3</sub> as an additive [Eq. (6-14)] (Ando et al., 1996; Sawamoto and Kamigaito, 1996b).

Similar living polymerizations of styrene were reported almost simultaneously and independently by another group (Wang and Matyjasewski, 1995a). The initiating system consists of 1-phenylethyl chloride, CuCl, and 2,2'-bipyridine, where the terminal C–Cl bond is reversibly and homolytically activated via the redox reaction of CuCl(I) complexed with the bipyridine to give polymers with narrow MWDs ( $\bar{M}_w/\bar{M}_n \sim 1.3$ ) in bulk at 130°C [Eq. (6-15)] (Wang and Matyjasewski, 1995a). A more judiciously designed





system,  $\text{PhEtBr/CuBr/4,4'-di-}n\text{-heptyl-2,2'-bipyridine}$ , affords much better controlled polymers with very narrow MWDs ( $\bar{M}_w/\bar{M}_n < 1.1$ ) (see below) (Patten et al., 1996). It has been proposed that these processes be called atom-transfer radical polymerizations (ATRPs) (Wang and Matyjasewski, 1995 a).

Although there have been no reports on the detection of the radical intermediate by ESR spectroscopy, these polymerizations most probably proceed via a radical pathway, as suggested by the following facts: Both the Ru(II)- and Cu(I)-based systems gave polymers with similar stereochemistry to those obtained with a conventional radical initiator like AIBN (Kato et al., 1995; Wang and Matyjasewski, 1995 a). The metal-catalyzed radical polymerizations were stopped by the addition of radical scavengers like galvinoxyl and TEMPO (Kato et al., 1995; Wang and Matyjasewski, 1995 a). The most distinguished finding may be that the ruthenium system induces smooth polymerizations even in the presence of methanol and water, which serve as terminators in ionic polymerizations, and gives living polymers with narrow MWDs ( $\bar{M}_w/\bar{M}_n \sim 1.2$ ) (Nishikawa et al., 1997). All the polymer chains possess the carbon-halogen bond at the  $\omega$ -terminal without it being converted into a carbon-metal bond (Ando et al., 1996; Wang and Matyjasewski, 1995 c), which supports the idea that the polymer-

ization proceeds via a radical mechanism and not via an ionic or an insertion mechanism.

### Design of Initiating Systems

The transition metal mediated systems discussed above involve multi-component initiating systems that consist of an initiator with a carbon-halogen bond, a metal complex, and sometimes an additive such as  $\text{Al(OiPr)}_3$ ; for example,  $\text{R-X/RuCl}_2(\text{PPh}_3)_3/\text{Al(OiPr)}_3$ . Figure 6-8 summarizes the components reported thus far.

The available transition metal complexes include not only  $\text{RuCl}_2(\text{PPh}_3)_3$  and  $\text{CuX}$  (with 2,2'-bipyridine;  $\text{X} = \text{Cl}, \text{Br}$ ), but also  $\text{FeCl}_2(\text{PPh}_3)_2$  (Ando et al., 1997),  $\text{NiBr}_2(\text{PR}_3)_2$  ( $\text{R} = \text{Ph}, n\text{Bu}$ ) (Uegaki et al., 1997),  $\text{Ni}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}]\text{Br}$  (Granel et al., 1996) and  $\text{RhCl}(\text{PPh}_3)_3$  (Percec et al., 1996). Thus the metal centers cover groups 8 to 11, all of which undergo reversible one-electron redox reactions with  $\text{C-X}$  bonds at the polymer terminals.

The polymerizations depend on the ligands on the complexes as well as on the central metals. Most typically, the heterogeneous polymerization with  $\text{CuX/2,2'-bipyridine}$  can be altered into a homogeneous one by introducing longer alkyl substituents like *n*-heptyl (Patten et al., 1996) and *n*-nonyl (Percec et al., 1996) groups at 4,4'-positions of the bipyridine, as is often done in the corresponding organic syntheses. The polymers obtained with the homogeneous copper-based system had very narrow MWDs, as described above (Patten et al., 1996). It has been reported that the copper-based system also needs a very small amount of  $\text{CuCl}_2(\text{II})$  ( $\sim 2$  mol% to  $\text{CuCl}$ ) for better controlled polymerizations (Patten et al., 1996). This may reduce the uncontrolled growing radical center by oxidizing it into the dormant  $\text{C-Cl}$  species.

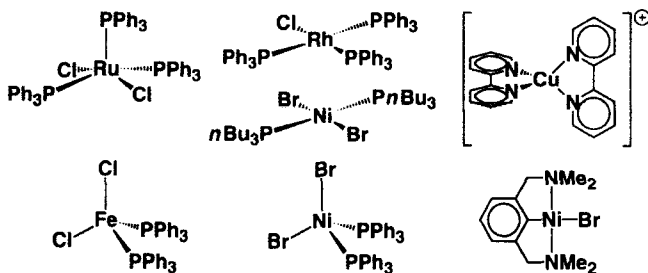
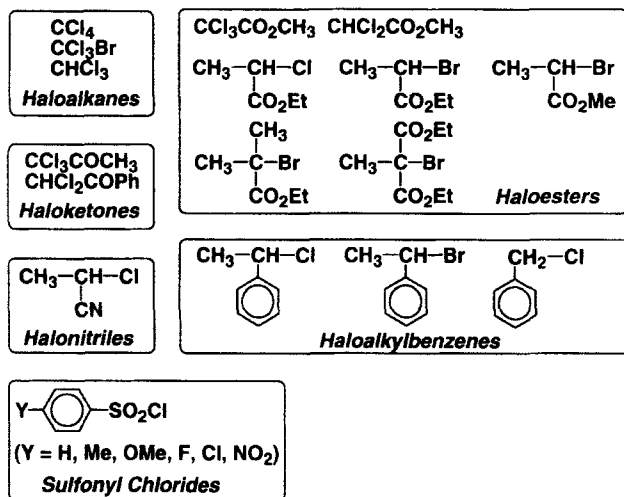
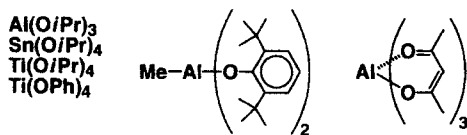
**Transition Metal Complexes:****Initiators:****Added Metal Compounds:**

Figure 6-8.

The added aluminum compounds in the ruthenium-mediated systems can be replaced with titanium(IV) and tin(IV) alkoxides (Ando et al., 1995; Sawamoto and Kanigaito, 1996b). These metal alkoxides were needed for increasing the polymerizations rate with  $\text{RuCl}_2(\text{PPh}_3)_3$  or  $\text{NiBr}_2(\text{PPh}_3)_2$ . They may interact with the ruthenium complex to change the redox potential of the metal center or, alternatively, they may activate the C–X bond via complexation on-

to the terminal ester group of the polymers. A plausible explanation of the role of the added compounds should be awaited. In contrast, the systems with  $\text{CuCl}$ ,  $\text{FeCl}_2(\text{PPh}_3)_2$ ,  $\text{NiBr}_2(\text{PnBu}_3)_2$ , or  $\text{Ni}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}o,o']\text{Br}$  do not need such added metal alkoxides.

The effective initiators include organic halides that almost invariably possess multiple chlorine atoms, carbonyl, or phenyl groups which stabilize radicals via inductive and/or resonance effects. Some systems fa-

vor a bromide initiator for better controlled polymerizations, probably due to the lower dissociation energy of the C–Br bond (Uegaki et al., 1997; Wang and Matyjaszewski, 1995 c). On the other hand, simple alkyl halides like *n*-butyl chloride cannot act as efficient initiators and result in uncontrolled polymerizations. Polyhalogeno compounds such as CCl<sub>4</sub> are effective initiators because of the inductive effects of plural chlorine atoms, but there is a possibility that they may act as multifunctional initiators or chain-transfer agents, although it has been confirmed that in Ru(II)/CCl<sub>4</sub> system the chloride was rapidly depleted in initiation during the very early stages of the polymerization (Kato et al., 1995).

In general, the excellent initiators are most likely the “unimer” counterparts for the dormant polymer terminal, for example, (CH<sub>3</sub>)<sub>2</sub>CBrCO<sub>2</sub>C<sub>2</sub>H<sub>5</sub> for methacrylates, CH<sub>3</sub>CHXCO<sub>2</sub>R (X=Cl, Br; R=Me, Et) for acrylates, and CH<sub>3</sub>CHXPh (X=Cl, Br) for styrene. However, some unimers were less efficient in some systems, because the reactivity of their C–X bond is lower than with polymers with high degrees of polymerization, thus the best may be the “dimer” counterparts. Arenesulfonyl chlorides also undergo Kharasch addition reactions in the presence of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> and CuX complexed with bipyridine (Asscher and Vofsi, 1964; Amiel, 1974; Kamigata, et al., 1983; Kameyama et al., 1987), and in fact serve as functional initiators for MMA (Matsuyama et al., 1996) and styrene (Perec and Barboiu, 1995; Percec et al., 1996) polymerizations.

Though mechanistically different, the AIBN/CuCl<sub>2</sub>(II)/2,2′-bipyridine system also induced controlled polymerizations of styrene (Wang and Matyjaszewski, 1995b; Gaynor et al., 1996b). The first step of this living polymerization is the formation of an initiating radical from AIBN and its addition to styrene, followed by the formation of the

covalent species with a C–Cl bond by the abstraction of chlorine from CuCl<sub>2</sub>, where the copper center is reduced from divalent to univalent. In contrast to the R–Cl/CuCl(I)/bipyridine system, the first step in this polymerization involves oxidation of the copper center from CuCl<sub>2</sub>(II) into CuCl(I). However, the subsequent polymerizations proceed via the same mechanism as the R–Cl/CuCl(I)/bipyridine system, where the catalyst is the univalent copper complex. The initiation efficiency of AIBN is nearly unity (0.95).

### Monomers

The transition metal catalyzed living radical polymerizations are applicable for various radically polymerizable monomers to give controlled molecular weights and MWDs ( $\bar{M}_w/\bar{M}_n=1.1-1.5$ ) (Kato et al., 1995; Ando et al., 1996; Kotani et al., 1996a, b; Wang and Matyjaszewski, 1995a, c). As listed in Fig. 6-9, the reported examples include methacrylates [CH<sub>2</sub>=C(CH<sub>3</sub>)CO<sub>2</sub>R; R=Me, Et, *n*Bu], acrylates [CH<sub>2</sub>=CHCO<sub>2</sub>R; R=Me, Et, *n*Bu], and styrenes [CH<sub>2</sub>=CH(*p*-R-C<sub>6</sub>H<sub>4</sub>); R=H, Me, Cl]. Relative to the TEMPO-based counterparts, the metal-mediated systems are apparently more versatile or less specific to the structure of monomers. For example, the Ru(II) and

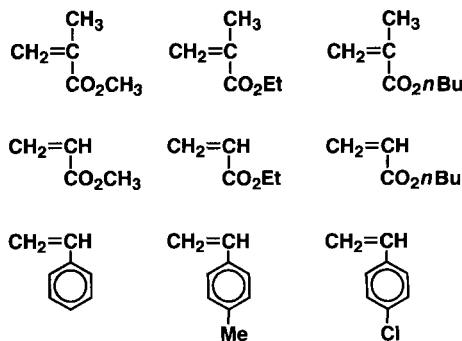


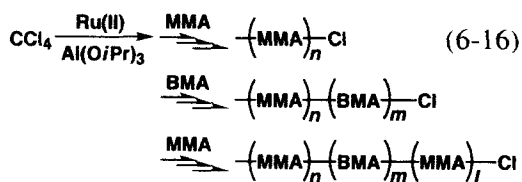
Figure 6-9.



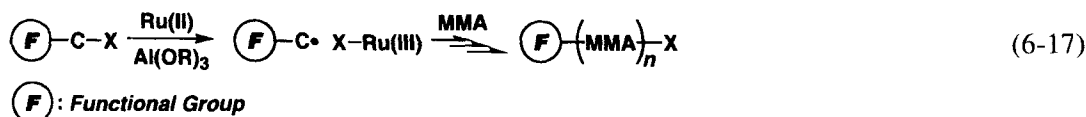
Cu(I) initiating systems are able to polymerize both methacrylates and styrenes; in contrast, TEMPO seems to work on styrene but not on methacrylates.

### Synthesis of Well-Defined Polymers

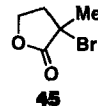
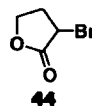
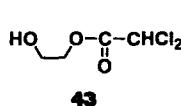
Because of the wide variety of applicable monomers for metal-catalyzed living polymerizations, several block copolymers have been prepared by sequential living polymerizations. For example, the ruthenium-based system gives diblock copolymers of MMA and BMA with narrow MWDs ( $\bar{M}_w/\bar{M}_n \sim 1.2$ ) by the sequential addition of BMA into the living poly(MMA) [Eq. (6-16)] (Kotani et al., 1996a). Further addition of MMA into the diblock MMA–BMA living polymers generates triblock copolymers of MMA–BMA–MMA ( $\bar{M}_w/\bar{M}_n \sim 1.3$ ). The copper-based system also leads to block copolymers of styrene and MA with  $\bar{M}_w/\bar{M}_n = 1.35$  (Wang and Matyjaszewski, 1995a). Thus many types of block copolymer have been synthesized using transition metal catalyzed living polymerizations.



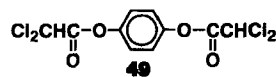
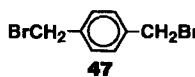
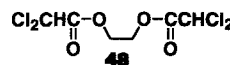
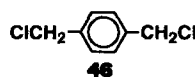
End-functionalized polymers have been prepared with functional initiators (**43**) that contain hydroxy groups in the ester moiety [Fig. 6-10 and Eq. (6-17)]. Halolactones like **44** and **45** are also available as functional initiators that produce polymers with a lactone unit at their terminals.



#### End-Functional



#### Bifunctional



#### Trifunctional

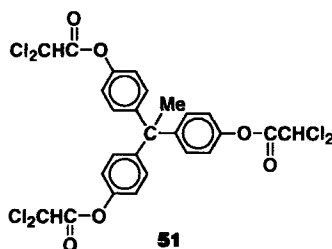
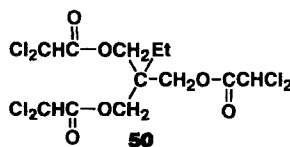


Figure 6-10.

The polyhalides where the halogens are separated by the use of an appropriate spacer act as well-defined multifunctional initiators (J. Ueda et al., 1996; Wang and Matyjaszewski, 1995c). For example, **46–49** serve as bifunctional initiators, and **50** and **51** as trifunctional counterparts.

The polymerization of *p*-chloromethylstyrene gave hyperbranched polymers where the benzylchloride part acts as the initiating point in conjunction with Cu(I) and bipyridine (Gaynor et al., 1996a). The hy-

perbranched structure has been confirmed by  $^1\text{H}$  NMR and SEC analyses. Copolymerizations of the monomer with styrene afforded another hyperbranched polymer with a looser structure.

As described above, transition metal catalyzed living radical polymerizations are apparently more applicable to a wide variety of monomers than the nitroxide-mediated counterparts at present. The transition metals serve catalytically, and the initiators that generate polymer chains are commercially available organic halides. The polymerization can be conducted in solution and at lower temperatures, often below  $80^\circ\text{C}$ , particularly with the use of efficient additives. However, it is still unknown whether the side reactions inherent to radical polymerizations are truly suppressed or not. Also, possible disadvantages may include lower reaction rates, the relative complexity of procedures because of the multicomponent initiating systems, and the resulting need to remove metal-containing residues from the products. As for future aspects, further design of the metal complexes including the ligands and the metal centers may make controlled polymerizations of other monomers possible, especially nonconjugating derivatives such as vinyl acetate, vinyl chloride, and other industrially important monomers. Another area of prime importance is of course stereospecific radical polymerizations, which seem inherently very difficult for conventional “free” radical processes.

#### 6.2.4 Carbon–Metal Bonds

Some transition metals form stable but potentially reactive covalent carbon–metal bonds directly with growing polymer terminals where the bonds can be reversibly cleaved by thermal or photochemical stimuli. Metals utilized for such controlled radical polymerizations include chromium,

rhodium, and cobalt [Eq. (6-9)]. The system based on the C–metal bond activation has similarities to both the C–halogen-based system with transition metal complexes and the C–ON-based system. The system involves one-electron redox reactions on the equilibrium between the dormant and activated species like the C–halogen-based system. The generating metal species on the reversible homolytic cleavage is per se stable like a nitroxyl radical generated in the C–ON-based system. However, the transition metal in this system is reduced on activation, and it does not serve in a catalytic way for the polymer chain, unlike in the case of the C–halogen-based system. In this sense, these systems (with carbon–metal bonds plus physical stimuli) are intermediate between the nitroxide systems (with carbon–heteroatom bonds plus physical stimuli) and the transition metal based systems (with carbon–heteroatom bonds plus chemical stimuli).

An excellent system based on this method is the living polymerization of MA with a cobalt(III) porphyrin (**52**) (Fig. 6-11) in benzene at  $60^\circ\text{C}$  (Wayland et al., 1994). The initiator, (tetramesitylporphyrinato)cobalt neopentyl [( $\text{CH}_3$ ) $_3\text{CCH}_2\text{--Co(TMP)}$ ], generates a stable Co(II)(TMP) species and a reactive carbon-centered neopentyl radi-

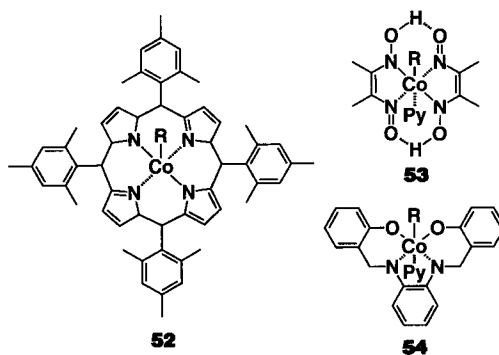


Figure 6-11.

cal. The carbon-centered radical adds to monomer to initiate the polymerization, whereas the Co(II) species reversibly forms a C–Co bond with the propagating radical via the redox reaction between Co(III) and Co(II). The produced polymers had molecular weights up to  $\bar{M}_n \sim 150\,000$ , which are controlled by the feed ratio of monomer to the cobalt complex, and very narrow MWDs ( $\bar{M}_w/\bar{M}_n \sim 1.2$ ). This system also affords the synthesis of block copolymers of MA and BA.

The use of the C–Co bond for organic synthesis (Pattenden, 1988) and radical polymerizations most likely originated from the chemistry of the coenzyme B<sub>12</sub>, where the cobalt center undergoes a similar redox reaction in metabolic processes. The success in living polymerization with the cobalt porphyrin is due to the stable Co(II) species, the low dissociation energy ( $\sim 80$  kJ/mol) of the C–Co bond (Woska et al., 1996), and the bulkiness of the porphyrin ligand. In contrast, the polymerization with similar cobalt complexes that possess smaller ligands like dimethylglyoxime (**53**) (Davis et al., 1995a) and salophen (**54**) (Banadaranayake and Pattenden, 1988) is not living because they are effective chain-transfer agents that abstract the  $\beta$ -hydrogen atom from the methylene group at the polymer terminal. Possible control of the stereoregularity has recently been investigated in the presence of the chiral cobalt(II) complex for MA polymerizations (Nakano et al., 1996).

In contrast to controlled acrylates polymerizations, the cobalt porphyrin complex is not effective for methacrylates, because the  $\beta$ -H abstraction from the  $\alpha$ -methyl group of the terminal gives the inactive hydride. A similar rhodium(II) porphyrin complex led to molecular weight increases in polymerizations of MA, but the MWDs were broader ( $\bar{M}_w/\bar{M}_n \sim 2$ ) (Wayland et al.,

1992). Cobaltocene [ $\text{Co}(\text{C}_5\text{H}_5)_2$ ] was employed for MMA in conjunction with bis(ethyl acetoacetato)copper [ $\text{Cu}(\text{eacac})_2$ ] (Mun et al., 1984a, b) and although the controllability is inferior to the porphyrin version this system can afford block copolymers of styrene and MMA (Mun et al., 1984b).

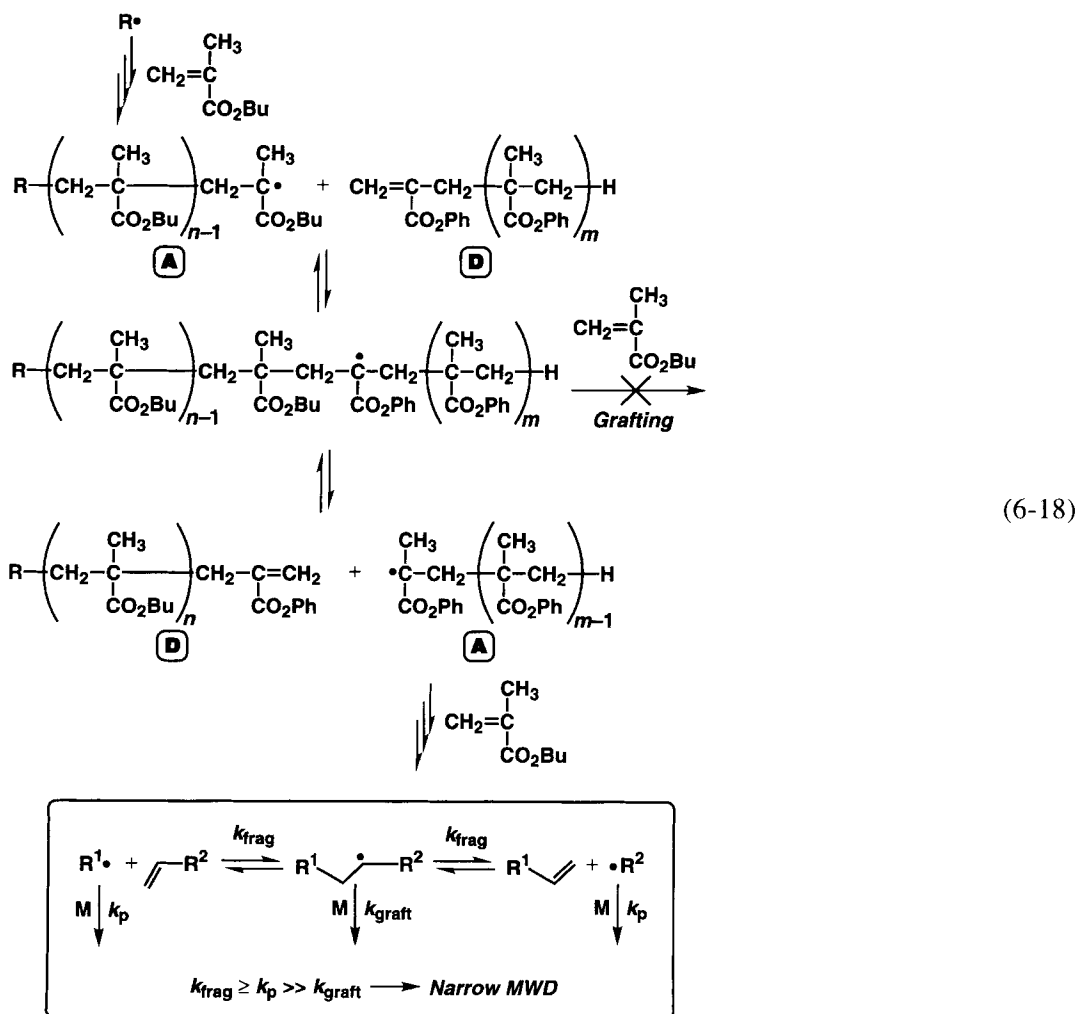
Although the degree of controllability is also a problem, the possibility of living radical polymerizations catalyzed by transition metals has been suggested perhaps for the first time for the polymerization of MMA with the aged complex of chromium(II) acetate [ $\text{Cr}(\text{OAc})_2$ ] and BPO in DMF at 30 °C (Lee et al., 1978). The polymerization was presumably initiated by the benzoyl radical generated from BPO and the Cr(II) compound during the aging at 10 °C, where the chromium center is reduced into the trivalent state. The interaction between the carbon-centered radical and the chromium center has not yet been clarified, but there is a possibility that the chromium center reversibly forms a C–Cr bond via redox reactions of the chromium center ( $\text{III} \leftrightarrow \text{IV}$  or  $\text{II} \leftrightarrow \text{III}$ ) (Gaynor et al., 1994). The polymerization rate and initiation efficiency can be increased with the use of aprotic solvents with high donor numbers, like HMPA or nitrogen ligands like phenanthroline and bipyridine (Lee et al., 1979, 1982). Recent reports also suggest the controlled polymerization of vinyl acetate using macrocyclic ligands like 1,4,7,10,13,16-hexaazacyclooctadecane trisulfate in conjunction with the BPO/Cr(OAc)<sub>2</sub> system (Gaynor et al., 1994).

### 6.2.5 Other Controlled Systems

As stated for the system using C–I bonds, degenerative transfer agents can control molecular weights and MWDs. Recently, it has been demonstrated that macromonomers with a  $\text{CH}_2=\text{C}(\text{CO}_2\text{R})\text{CH}_2-$

group can serve as efficient addition–fragmentation chain-transfer agents in the radical polymerization of methacrylates to form block copolymers with controlled molecular weights and narrow MWDs ( $\bar{M}_w/\bar{M}_n \sim 1.4$ ) (Kristina et al., 1995). This controlled polymerization proceeds as if the  $\text{CH}_2=\text{C}(\text{CO}_2\text{R})\text{CH}_2$ -terminal were the dormant species, like the C–I species. As shown in Eq. (6-18), block copolymers can be attained from the phenyl methacrylate (PhMA) macromonomer and the BMA monomer by this method. Thus a small amount of propagating radical species of

BMA units, originally generated from conventional radical initiators like  $\text{K}_2\text{S}_2\text{O}_8$ , reacts with the  $\text{CH}_2=\text{C}(\text{CO}_2\text{Ph})\text{CH}_2$ -group to form an adduct with a mid-chain radical. The adduct does not produce graft copolymers by reacting with BMA but undergoes fragmentation to regenerate the two starting compounds or to give a new PhMA propagating species and a BMA macromonomer with a  $\text{CH}_2=\text{C}(\text{CO}_2\text{Ph})\text{CH}_2$ -group. The PhMA propagating species subsequently reacts with the BMA monomer and then combines again with the BMA or PhMA macromonomer. Such a sequence of addi-



tion fragmentation and propagation eventually leads to block copolymers. The chain-transfer constants of the macromonomers with certain chain lengths were obtained, and their chain-length dependence was discussed (Moad et al., 1996). In this process, the fast and reversible addition–fragmentation reaction ensures controlled molecular weights by the feed ratio of BMA monomer to PhMA macromonomer and narrow MWDs, as in the radical polymerizations using alkyl iodides as degenerative transfer agents.

Another approach to living radical polymerizations is stabilization of the radical species itself via interaction with a  $\pi$ -donor. The addition of tetrathiafulvalene (**55**) (Fig. 6-12) narrowed the MWDs of poly(MMA) from 2.6 to 1.5 in the polymerization with AIBN at 60°C (Wunderlich et al., 1996). The absence of irregular structures due to bimolecular termination (disproportionation and recombination) was indicated by the TG analysis of the products. This suggests that the propagating radical species are shielded by the  $\pi$ -donor. Such interactions have also been investigated by ESR analysis on the polymerization of MMA with AIBN in the presence of diphenylacetylene (**56**) (Hwang and Ogawa, 1990). Such a living polymerization based on organic  $\pi$ -donor-induced stabilization is of interest because of the possible existence of the truly stabilized radical species that can completely elude side reactions.

All the above-mentioned systems are based on the chemical stabilization of radical species. Quite different stabilization can

be accomplished by the physical stabilization of radical species using micelles and zeolites. Polymerizations by this method are summarized elsewhere (Tanaka, 1992), and the details are omitted in this review. More recently, there was a report on the control of molecular weight by the size and length of nearly uniform-sized mesoporous zeolites (Ng et al., 1996). The stability of the propagating radical species in the mesopore is supported by the ESR studies. The molecular weights seemed to be controlled by the length of the mesopore, though the MWDs were broad ( $\bar{M}_w/\bar{M}_n = 1.7-6$ ). Evidently, the use of mesopores is intended to isolate the growing “free” radicals from each other to suppress bimolecular termination while keeping a relatively large space around the growing end, so that monomers can move into the active sites.

### 6.3 Concluding Remarks

As discussed in this article, it becomes increasingly evident that radical polymerizations can be controlled by the use of carefully designed initiating systems. Most of the living or controlled radical polymerizations involve the fast equilibrium between the reactive radical species and the dormant species with a potentially active covalent bond, where the equilibrium is shifted to the latter. Table 6-1 summarizes the characteristics of representative living or controlled radical polymerizations of commercially available monomers like MMA, MA, and styrene in terms of the bonds and stimuli for radical generation, the polymerization temperature, and the polymer MWDs. Apparently, some systems cannot be available for certain monomers, because the nature of the carbon-centered radicals differ in each monomer and accordingly affects the efficiency of the radical-capping reactions and

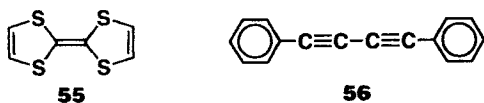


Figure 6-12.

**Table 6-1.**  $\sim\sim\sim\text{C}-\text{Y} \xrightleftharpoons{\text{Stimuli}} \sim\sim\sim\text{C}^{\bullet} + \cdot\text{Y}$

$\sim\sim\sim\text{C}-\text{Y}$	Stimuli	Temp.	Monomer	$\bar{M}_w/\bar{M}_n$
$\sim\sim\sim\text{C}-\text{CPh}_3$	$\Delta$	60–90°C	MMA, St	$\geq 1.5$
$\sim\sim\sim\text{C}-\text{S}$	$h\nu$	30°C	MMA, St	$\geq 1.5$
$\sim\sim\sim\text{C}-\text{ON}$	$\Delta$	90–130°C	St	1.1–1.2
$\sim\sim\sim\text{C}-\text{I}$	$\text{R}^{\bullet}$	60–80°C	St, VAc	$\geq 1.3$
$\sim\sim\sim\text{C}-\text{X}$ (X=Cl, Br, I)	metal	60–130°C	MMA, MA, St	1.1–1.2
$\sim\sim\sim\text{C}-\text{Co}$	$\Delta$	60°C	MA	1.1–1.2

the stability of the dormant species. The kinds of monomers thus far polymerized with nearly perfect control ( $\bar{M}_n \sim 100\,000$ ,  $\bar{M}_w/\bar{M}_n \leq 1.2$ ) are restricted to styrenes, methacrylates, and acrylates. Thus far, no system has succeeded in the well-controlled radical polymerization of other radically polymerizable and commercially available monomers like vinyl acetate, (meth)acrylonitrile, (meth)acrylamide, vinyl chloride, butadiene, ethylene, etc. The studies on controlled radical polymerizations are still developing and will be applied for such monomers in the near future. The mechanism of living radical polymerizations will also be clarified further.

Such a design of polymerization systems based on the reversible formation of reactive growing species from the dormant species is not specific to the radical pathways but it is, apparently, specific to other mechanisms, including living anionic polymerizations of (meth)acrylic monomers and living cationic polymerizations of vinyl monomers, where the actual growing species are susceptible to side reactions (Webster, 1991; Aida, 1994; Hirao and Nakahama, 1994; Sawamoto, 1993; Kennedy, 1995; Hsieh and Quirek, 1996; Matyjaszewski and Sawamoto, 1996; Breslow, 1993; Sawamoto and Higashimura, 1989; Kennedy and Iván, 1992). For example, there are similarities between the radical living polymerizations based on C–halogen activation by

transition metal complexes and those of the cationic counterparts with Lewis acids (Kamigaito et al., 1993). The former system involves reversible and homolytic cleavage of the C–halogen bonds, whereas the latter involves reversible but heterolytic cleavage. The cobalt porphyrin-mediated radical living polymerization of acrylates is similar to the aluminum porphyrin-mediated anionic living polymerization of methacrylates, because both involve the equilibrium between the dormant species with covalent C–metal and O–metal bonds, respectively, which are converted into reactive growing polymer terminals and metal porphyrins (Aida and Inoue, 1996). The sterically large porphyrin ligands are crucial in both controlled polymerizations.

From another view point of controlling the polymer structure, stereocontrol is one of the most important targets. Stereocontrol has already been accomplished in coordination olefin polymerizations with Ziegler–Natta and Kaminsky-type catalysts (Binzinger et al., 1995; Bochmann, 1996), anionic living polymerizations of acrylates with elemental metals (Kitayama et al., 1990), lanthanoid-mediated living polymerization of methacrylate (Yasuda and Tamai, 1993), etc. In the olefin polymerization with metallocenes, it has recently been suggested that the structure of the dormant species plays important roles in determining the steric structure of the product polymers.

Thus the existence of the covalent dormant species is the key for controlled polymerizations in terms of steric structure as well as molecular weight and other structural parameters. As described above, the control of stereoregularity in radical polymerizations was attempted for some monomers (Puts and Sogah, 1996; Nakano et al., 1996), but has not been achieved yet. This may be accomplished in future by introducing bulky or chiral groups into the counter radical compounds.

Also, the above-mentioned similarities in mechanism, or more precisely, in principles for reaction control, may increasingly blur the traditional classification of polymerization mechanisms and make them less important. It is therefore hoped that success and further generalization in living or controlled radical polymerizations will therefore help establish general concepts and principles for the precise control of addition polymerizations as a whole.

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## 7 Anionic Polymerization: Recent Advances

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## List of Symbols and Abbreviations

$\log_{10}A$	preexponential factor
$DP_n$	number average degree of polymerization
$E_a$	activation energy
$h$	Planck constant
$pK_a$	negative logarithm of equilibrium constant for association
$K_{eq}$	equilibrium rate constant
$k_p$	propagation rate constant
$m$	number
$M_n$	number average molecular weight
$M_w$	weight average molecular weight
$M_w/M_n$	polydispersity index
$n$	number
$r$	reactivity ratio
$T_g$	glass transition temperature
$x$	number
$y$	number
$\nu$	frequency
Ac	acetyl
acac	acetylacetonate (-o)
AIBN	azobisisobutyronitrile
B (BD)	butadiene
CE	crown ether
CHx	cyclohexane
DIB	1,3-diisopropenylbenzene
DME	ethylene glycol dimethyl ether
DMF	<i>N,N</i> -dimethylformamide
DPE	diphenylethylene
DPMLi	diphenylmethyllithium
EtA	ethyl acrylate
2EtHA	2-ethylhexyl acrylate
GTP	group transfer polymerization
H	high molecular weight
HMPA	hexamethylphosphoramide
Hp	high molecular weight (after polymerization)
L	low molecular weight; ligand
LAP	“ligated” anionic polymerization
LiOE <sub>2</sub> M	lithium 2-(2-methoxyethoxy) ethoxide
Lp	low molecular weight (after polymerization)
M	metal; MMA; <i>t</i> BuMA
MALDI – TOF	matrix-assisted laser desorption ionization – time of flight
Me	methyl
MeA	methyl acrylate

MIBLi	methyl $\alpha$ -lithioisobutyrate
MMA	methylmethacrylate
Mt	metal
MTS	1-methoxy-2-methyl-1-trimethylsiloxypropene
MW	molecular weight
MWD	molecular weight distribution
<i>n</i> BuA	<i>n</i> -butylacrylate
NMR	nuclear magnetic resonance
Nu	nucleophile
PBD	polybutadiene
PCL	polycaprolactone
Ph	phenyl
PMMA	poly(methylmethacrylate)
Pr	propyl
PS	polystyrene
PVA	polyvinylalcohol
R	alkyl
S	styrene
SAP	screened anionic polymerization
SBS	styrene–butadiene–styrene triblock copolymer
SEC	size exclusion chromatography
TAS <sup>(+)</sup>	tris(dimethylamino) sulfonium ion
TASF	tris(dimethylamino) sulfonium fluoride
TASHF <sub>2</sub>	tris(dimethylamino) sulfonium bifluoride
TASMe <sub>3</sub> SiF <sub>2</sub>	tris(dimethylamino) sulfonium difluorotrimethylsiliconate
TBAMF	tetrabutylammonium methylfluorenyl
<i>t</i> BIBLi	<i>tert</i> -butyl $\alpha$ -lithioisobutyrate
<i>t</i> BuA	<i>tert</i> -butylacrylate
<i>t</i> BuMA	<i>tert</i> -butylmethacrylate
THF	tetrahydrofuran
Tol	tolyl
TPP	tetraphenyl porphyrin
UV	ultraviolet

## 7.1 Introduction

The development of anionic chemistry over the past four decades has led to the emergence of new polymeric processes and products of industrial importance, the most significant being the family of thermoplastic elastomers. These unique elastomers are presently commercialized by the Shell Chemical Company as Kratons and by the Phillips Chemical Company as Solprenes. Their phenomenal growth in commercial production can be attributed to the unprecedented control the anionic process provides over the polymer properties, i.e., deliberate design of the polymeric structure and composition.

The impressive advances in anionic polymerization stem from the early work of Szwarc and co-workers in 1956 on the so-called "living" polymerization (Szwarc et al., 1956). These living systems, resulting from propagation free of termination and chain transfer, make macromolecular engineering possible; this is defined as the synthesis and characterization of polymers exhibiting well-defined molecular structures, low compositional heterogeneities, and narrow molecular weight distributions. These well-tailored polymers have also led to detailed and deep understanding of the mechanism of ionic polymerization, because the stability of the growing end groups permits the chemists to examine their nature and the modes of their reactions. Not surprisingly, these developments had, and continue to have, a striking impact on progress in other fields of polymer chemistry and physics, as well as in the advancement of polymer engineering and technology.

It is out of the scope of this chapter to cover the literature on anionic living polymerization exhaustively; several excellent reviews and books dealing with the kinetics, thermodynamics, and mechanisms of anion-

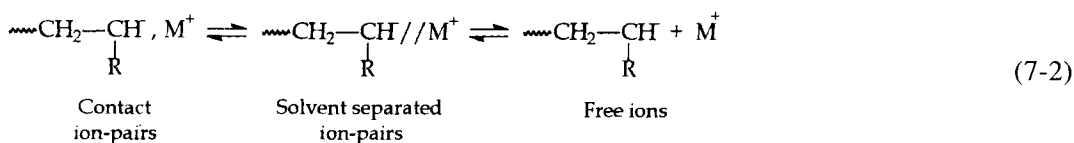
ic polymerization are already available (McGrath, 1981; Young et al., 1984; Van Beylen et al., 1988; Szwarc and Van Beylen, 1993; Hsieh and Quirk, 1996; Szwarc, 1996). Emphasis will instead be on very recent developments in anionic living polymerization and especially in the polymerization of polar unsaturated monomers, such as (meth)acrylic esters, since the most remarkable progress has been made in this area in the last decade. Before discussing the recent strategies investigated in order to get better control in anionic polymerization, we will briefly survey the main characteristic features of "livingness" in anionic polymerization.

## 7.2 General Aspects of Anionic Living Polymerization

The chief feature of anionic living polymerizations in aprotic solvents is that they involve only two reactions: initiation and propagation. Spontaneous transfer or termination reactions will not take place if proper systems and adequate reaction conditions are chosen. As a consequence, molecular weight control is easy to achieve, provided initiation is fast with respect to propagation. The number average degree of polymerization is given by the monomer consumed to initiator molar ratio

$$DP_n = \frac{\Delta [M]}{[I]} \quad (7-1)$$

Furthermore, the reaction scheme implies that the molecular weight distribution is Poisson-like, i.e., very narrow, as has been shown elsewhere on a theoretical basis by Flory (1940). Even though two (or more) types of active species add monomer at very different rates, the polydispersity remains narrow, provided the solvation/desolvation and ionic dissociation/association processes are fast (Figini, 1967)



It is interesting here to compare the anionic and radical modes of polymerization. Radical polymerization is initiated by the addition reaction of a monomer onto a radical moiety formed by the homolytic cleavage of a suitable initiator. The added radical is found attached to the growing polymer chain as the tail group, but its nature, and therefore the nature of its precursor, does not influence the kinetics or the (stereo)selectivity of the propagation step. These characteristics are actually dependent upon the nature of the monomer, the temperature of the free radical polymerization, and, to a lower extent, the nature of the solvent. In contrast, the mode of anionic propagation is affected substantially by the nature of the initiator, since its counterion remains associated in some manner with the growing active site [see Eq. (7-2)]. The active propagating groups may exist as ion-pairs, which can be solvated and even dissociate into free ions. All these species are in equilibrium and, since the observed kinetics and mechanism of polymerization depend on their relative content in the reaction medium, the course of anionic polymerization is more complex, but also more versatile, than that of radical polymerization.

The bimolecular termination through the coupling or disproportionation of two free radicals makes their lifetime very short, often less than a few seconds. This accounts for the almost constant molecular weight of the resulting polymer chains, independent of the degree of monomer conversion. The inevitability of the bimolecular termination is also responsible for a drastic limitation of the radical concentration. Their stationary concentration barely exceeds  $10^{-4}$  M, so

that most of the macromolecules present in a radical polymerization are dead. Only a minute fraction of them contributes to the propagation at any time. However, it is worth pointing out the very recent breakthrough achieved in the field of controlled/"living" radical polymerization, which allows for the synthesis of well-tailored poly(meth)acrylic and polystyrenic derivatives. Purposely, the radical chain termination, i.e., recombination and disproportion, might be suppressed, or at least drastically reduced, by generating growing species where the growth active radical species is in a rapidly exchanging equilibrium with a stable dormant counterpart. Current literature shows that there are, among others, two major strategies to achieve "living" radical polymerization: one with a stable radical end-capper, e.g., nitroxyl-type radicals (Georges et al., 1994; Hawker, 1996), and the other with metal complexes as a component of the initiating systems (Sawamoto and Kamigaito, 1996; Patten et al., 1996). In the second approach, for instance, the active radical species is in a rapidly exchanging equilibrium with a halogen-capped covalent counterpart. If the dormant carbon-halogen terminal linkage can be homolytically and reversibly cleaved, and if the equilibrium is favored for the dormant side, then the instantaneous concentration of the growing radical end will be extremely low so as to suppress the bimolecular termination reactions.

During most of the anionic polymerization, collision of the active ionic species does not annihilate them and consequently does not destroy their capacity to grow further. In fact, the concentration of growing

polymers can be as high as  $10^{-2}$  M in anionic polymerization (Szwarc and Van Beylen, 1993). Thus, in numerous anionic polymerizations, it is possible to avoid termination and chain transfer. Different synthetic strategies have been investigated to obtain the "livingness" of the process. As we will report in the following sections, the nature of the counterion, the addition of coordinative ligands, the polarity of the aprotic solvent, and the polymerization temperature constitute key parameters which have to be taken into account. Indeed, as remarked earlier, the end groups of anionic living polymers exist in a variety of distinct forms, the relative content of which depends on the aforementioned parameters. For example, in addition to the equilibrium between free ions and ion-pairs, aggregates of polymers remain in equilibrium with the nonaggregated ones, covalently and ionically bonded species may be in equilibrium with each other, and so forth. The propagation constant of each of these species is different, and for some might be virtually zero. Although the latter do not contribute directly to the propagation, they are not dead either, since a spontaneous and reversible interconversion transforms them into the propagating polymers. Such temporary, inactive species are usually referred to as dormant polymers. The span of their dormancy is determined by the reciprocal of the rate constant to their conversion into the active form, which in turn is strongly affected by the polymerization conditions, e.g., concentration, polarity and temperature of the reaction medium, addition of complexing agents, nature of the counterion and monomer, etc.

To be eligible for living anionic polymerization, a vinylic monomer should carry an electron-attracting substituent to induce polarization of the unsaturation. However, it should contain neither acidic hydrogen nor a strongly electrophilic function which could

induce deactivation or side reactions. Typical examples of monomers suited to be anionically polymerized in a living manner are: substituted or unsubstituted styrene, vinylpyridine, conjugated dienes, alkyl (meth)acrylates, and also monomers with protected hydrogen-containing functions. For instance, hydroxyethylmethacrylate and glyceryl methacrylate can undergo anionic polymerization as silyl-ether or -acetal, respectively. After polymerization, the alcohol functions are recovered by mild acid hydrolysis (Rempp et al., 1988).

Living systems imply the occurrence of microreversibility, i.e., propagation/depolymerization reactions (Brown and Szwarc, 1958). However, for practical reasons, the equilibrium monomer concentration is generally very low, and quantitative conversions can be attained. There are nevertheless, a number of 1,1-disubstituted monomers, such as  $\alpha$ -methylstyrene, in which propagation/depolymerization equilibria trigger a lowering of the yields and a broadening of the molecular weight distributions. In these cases, it is necessary to operate at a low temperature (although the reaction is then quite slow) and to deactivate the anionic species at a stage where the equilibrium is still far from being reached (Rempp et al., 1988).

Anionic living polymerization thus provides the synthetic polymer chemist with perfect control of the molecular parameters of the produced polymers. The preparation of block copolymers, free of homopolymers, having the desired sequence and size of blocks, is probably the major application, but the synthesis of functionalized polymers also arises directly from the long lifetime of the active sites. The reactivity of the end groups permits their conversion into the required functional groups so that  $\alpha$ - or  $\omega$ -functional (telechelic) polymers are made available. By this procedure, macro-

monomers can be produced, i.e., linear polymers fitted at a chain end with a polymerizable unsaturation, most commonly styrene or a (meth)acrylic ester. These species in turn provide easy access to graft copolymers upon radical copolymerization with vinylic or acrylic comonomers. The use of linking or coupling agents allows the conversion of bifunctional linear living chains into macrocyclics. A modification of these procedures yields star-shaped and comb-like polymers. The successful contribution of anionic polymerization to macromolecular engineering has been elegantly reviewed by Rempp et al. (1988).

Before discussing the most recent advances achieved in anionic living polymerization, it is worthwhile recalling that “living polymers are not immortal”, as pointed out by Szwarc in his very first paper introducing the concept of living polymers (Szwarc, 1956). It is indeed inconceivable for propagation to proceed indefinitely with the rigorous exclusion of termination and chain transfer. With time, any living chain eventually decomposes, isomerizes, or reacts with its surroundings. Therefore Szwarc suggested that the first condition had to be relaxed to the point where a polymer could be referred to as living if the end groups retain the propensity of growth for at least as long a period as needed for the completion of an intended synthesis (Szwarc, 1992). In other words, a maximum molecular weight polymer should be obtained without being interrupted by termination or chain transfer. In fact, even this requirement could be relaxed. Szwarc and Van Beylen (1993) recently wrote: “One is often satisfied if not more than say 2% of the growing species are terminated, or undergo chain-transfer, when polymers of the demanded size are formed”.

## 7.3 Strategies

As already emphasized, the most recent progress achieved in the field of anionic living polymerization deals with the tailoring of poly(meth)acrylic esters derivatives. Until about the late 1970s, perfectly controlled polymerization of alkyl acrylates and methacrylates had been a permanent, but poorly answered challenge in polymer science. And yet the incentives were huge and numerous, i.e., increasing availability of the corresponding monomers (production nowadays approaching  $6 \times 10^6$  tonne per year), versatility of the obtained materials, including plastics, fibers, adhesives, and elastomers, which may contain a number of different reactive functions, and a higher usage temperature, e.g., by increasing  $T_g$  to 130 °C or higher for poly(methylmethacrylate) (PMMA) having a syndiotactic content of at least 80%.

Methacrylates and acrylates are traditionally polymerized by free radical techniques. Even though the versatility of this synthetic route has been exploited for industrial purposes, ranging from bulk polymerized optically transparent materials to paints and surface coatings, a more controlled method of polymerization has been demanded. The conventional anionic initiators, and more particularly *sec*-butyllithium, have long proven very efficient in the controlled polymerization of styrenes, conjugated dienes, and other vinylpyridines. However, the anionic living polymerization of (meth)acrylic esters was barely achieved. There were essentially two problems:

- 1) Poor selectivity of the nucleophilic addition; the expected Michael 1,4-addition was contaminated by a 1,2-attack on the carbonyl group and, to a lesser extent, by an acid–base reaction with the hydrogen atom in the  $\alpha$ -position of the carbonyl



function. The major mechanism for termination under normal experimental conditions is an intramolecular reaction, i.e., a back-biting reaction, yielding a six-membered ring with the evolution of alkoxide ions (for further discussion, see Sec. 7.4.1).

- 2) A coordinative aggregation of the anionic active sites, either alkylmetal or enolate, i.e., formation of  $\mu$ -type complexes. The tendency to aggregate is more pronounced in less polar solvents.

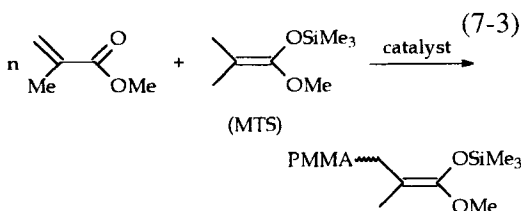
Several (partially) successful strategies have been followed in order to gain control over the polymerization process in terms of the molecular weight (MW), the MW distribution (MWD), the stereochemistry, and the process "livingness" (necessary for the tailoring of the chain architecture and the introduction of functionality). As imposed by the electron-withdrawing ester substituent, all of these strategies have logically called for nucleophilic processes and may be categorized as follows:

- 1) Group-transfer polymerization, as proposed by DuPont (Webster et al., 1983; Sogah et al., 1987).
- 2) Metal-free anionic polymerization: use of all-organic large and delocalized ion-pairs (Reetz, 1988; Sivaram et al., 1991).
- 3) Nucleophilic/coordinative polymerization (Collins and Ward, 1992; Yasuda et al., 1993) and the metalloporphyrin-mediated polymerization proposed by Inoue et al. (1990).
- 4) "Ligated" anionic polymerization studied by several research groups depending on the nature of the added ligand:  $MR_n$  (Hatada et al., 1986),  $R_nMOAr$  (Ballard et al., 1992), MOR (Lochmann et al., 1974, 1979), and LiCl, hindered crown ether, and  $LiOE_nR$  developed by our group (Fayt et al., 1987; Varshney et al., 1990a, 1992; Bayard et al., 1994).

These different methods will be discussed in turn.

## 7.4 Group Transfer Polymerization

In 1983, Webster and his co-workers at DuPont reported a new living polymerization method called group transfer polymerization (GTP) for acrylic monomers, especially methacrylates (Webster et al., 1983). It involves the catalyzed addition of the monomer to a growing polymer chain end which carries a reactive silyl ketene acetal group. During the addition, the silyl group transfers to the incoming monomer, regenerating a new ketene acetal function ready for reaction with more monomer [see Eq. (7-3)], hence the name group transfer polymerization (Webster, 1987)



The group transfer process involves a silyl ketene acetal initiator, most commonly 1-methoxy-2-methyl-1-trimethylsiloxypropene (MTS), which on its own is inactive. MTS only initiates polymerization in the presence of a catalyst, which may be either a nucleophile or a Lewis acid (Sogah and Webster, 1983). The degree of polymerization is dictated by the monomer-to-initiator molar ratio and is independent of the catalyst concentration, which, however, affects the propagation kinetics (Mai and Müller, 1987; Brittain, 1988). Nucleophilic catalysts such as soluble fluoride, bifluoride, azide, and cyanide are usually introduced as salts of an organic cation, e.g., the tris(dimethylamino) sulfonium or tetrabutylam-

monium ion. Electrophilic catalysts include zinc halides, alkylaluminum chlorides, and alkylaluminum oxides (Hertler et al., 1984). However, nucleophilic catalysts are preferred because only small amounts are needed, typically 0.12 mol% based on the initiator. On the other hand, electrophilic catalysis require as much as 10% catalyst, based on the monomer. Note that more recent evidence has shown that 1% catalyst, especially for  $\text{HgI}_2$ , could be sufficient (Zhuang and Müller, 1995).

Typical solvents include toluene, tetrahydrofuran (THF), and *N,N*-dimethylformamide (DMF) for nucleophilic catalysis, and toluene and dichloromethane for Lewis acid catalysis.

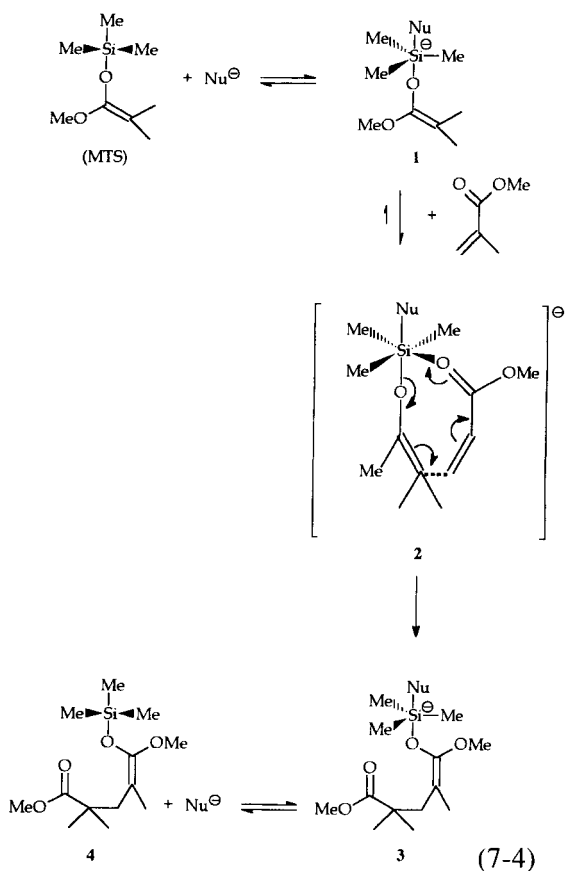
The polymerization of methacrylates yields polymer with a predictable molecular weight and narrow polydispersity index ( $M_w/M_n < 1.2$ ). In contrast, the  $M_w/M_n$  broadens for acrylate polymerization. Note that functional groups sensitive to free radicals, such as allyl or sorbyl, can be present on the ester groups of the monomer and remain unreacted in the polymer (Webster, 1987).

GTP was a significant new development, since it combined the important advantages of living polymerization with the ability to carry out polymerization at room temperature and above (ca. 80°C). This was an improvement over classic anionic living polymerization, which requires a low temperature ( $\leq -60^\circ\text{C}$ ) for its successful operation.

The mechanism of GTP has been the subject of considerable debate, and various approaches have been made in order to understand it.

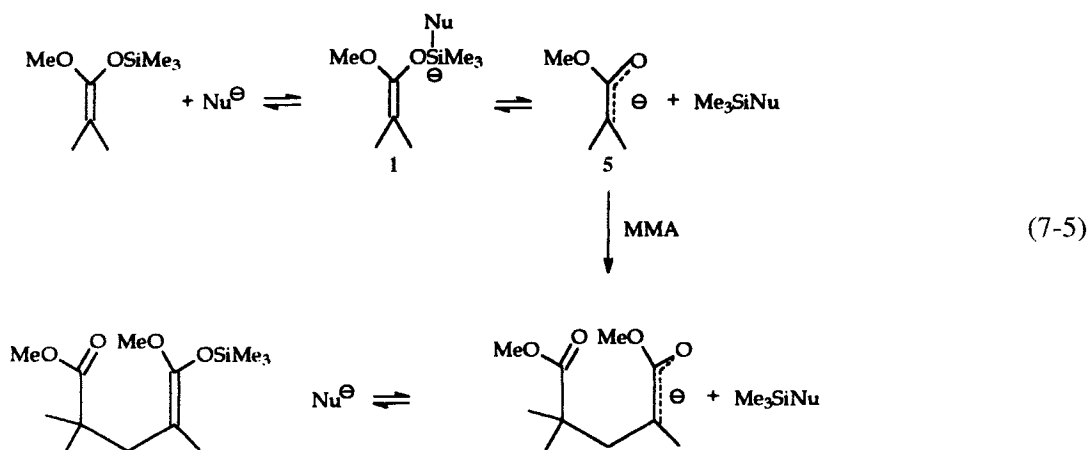
#### 7.4.1 A Discussed Mechanism

The mechanism of GTP proposed in the original papers of the DuPont team is depicted in Eq. (7-4).



The nucleophilic catalyst, e.g.,  $\text{HF}_2^-$ , coordinates with the silicon atom of the initiator (MTS) to provide a pentacoordinate species **1**. The activated initiator and monomer (MMA, for instance) were proposed to form a hexacoordinated (hypervalent) silicon intermediate **2** and a rather unusual eight-membered ring transition state. A new carbon-carbon bond is created between the initiator and monomer, and the trimethylsilyl group is transferred to the carbonyl oxygen of the monomer. The structure of **4** is therefore similar to that of the initiator (MTS) (Sogah and Farnham, 1985).

This mechanism, known as the associative one, could be treated as a pseudoanionic process, since propagation results from the insertion of a monomer caused by the rearrangement of covalent bonds, and not from

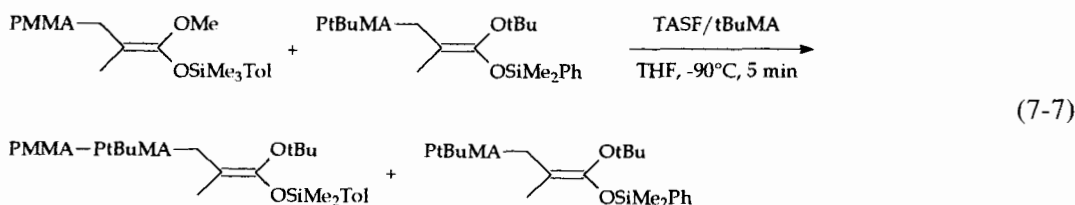
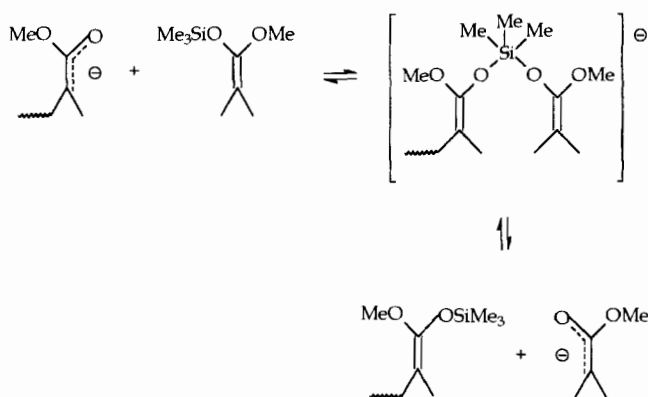
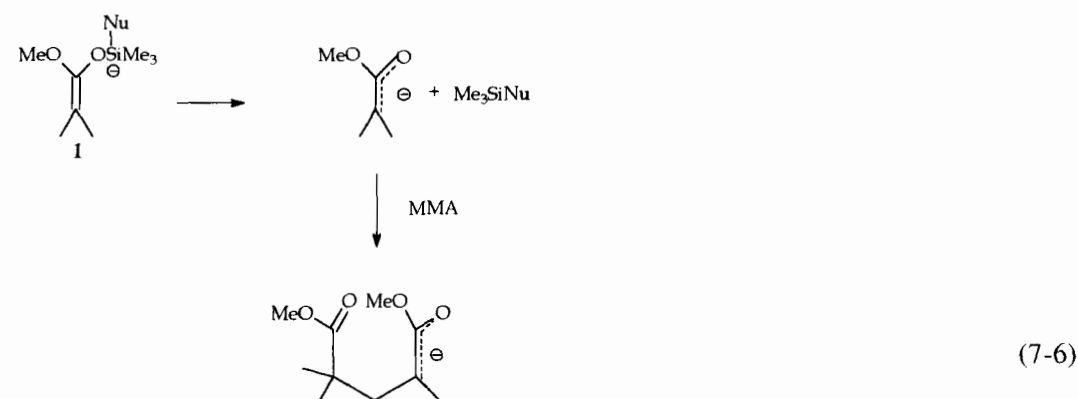


the addition to an ion. This mechanism does not involve dissociation of the activated silylketene acetal and a silane. However, such a “dissociative” mechanism [Eq. (7-5)] was plausible, as Noyori et al. (1983) had reported that enolates may be produced from the reaction between silyl enol ether and a fluoride ion source. Accordingly, the enolate **5** [Eq. (7-5)], capable of adding the monomer, is formed by dissociation of complex **1**, so releasing the  $\text{Me}_3\text{SiNu}$  fragment. The nucleophile accelerates the formation of the enolate. Note that next to this so-called reversible dissociative mechanism, the  $\text{Me}_3\text{Si}$  moieties can also be expected to be exchanged rapidly between the different polymeric chains, i.e., an irreversible dissociative mechanism with a transfer of propagation from one chain to another [Eq. (7-6)] (see Davis et al., 1994).

The double-labeling experiments reported by Sogah et al. (1987) demonstrated that the silyl groups were not exchanged between different polymer chain ends. A mixture of living PMMA and living poly(*tert*-butylmethacrylate) (*t*BuMA) chains with dimethyltolylsilyl and dimethylphenylsilyl ketene acetal end groups, respectively, was used to initiate the polymerization of *t*BuMA in the presence of TASF as a catalyst [Eq. (7-7)]. After 5 min in THF at  $-90^\circ\text{C}$ , the

polymerization was quenched and the two polymers separated by solubility, i.e., one homo P(*t*BuMA) and the other a block copolymer of *t*BuMA and MMA. The exclusive isolation of these two polymers showed that there had been no exchange of end groups, thereby precluding the dissociative mechanism.

The “associative” mechanism was also confirmed by the unsuccessful attempts to trap the  $\text{Me}_3\text{SiNu}$  intermediate which would be produced according to Eqs. (7-5) and (7-6) (Sogah and Farnham, 1985). However, the kinetics and tacticity measurements performed by Müller and co-workers (Müller and Stickler, 1986; Mai and Müller, 1987) provided evidence for a monomer addition occurring through a two-step process rather than in a concerted manner. For instance, the Arrhenius plots derived from the kinetics study of the group transfer propagation of methyl and *t*-butylmethacrylate are significant. The kinetic data, such as the activation energy, the preexponential factor, and the propagation rate constant of GTP are very similar to those obtained for classic anionic polymerization, particularly when large counterions were used (Table 7-1). In the latter case, the monomer addition proceeds via a direct attack of the carbanion on the monomer vinyl group, similar to radical poly-



merization. Coordination of the monomer carbonyl group to the hypervalent silicon atom simultaneous with the vinyl addition [cf. Eq. (7-4)] should result in much higher activation entropies (corresponding to lower frequency exponents) than those observed in anionic polymerization (Müller, 1990). Consequently, it seems more likely that monomer addition is a two step process.

It is also worth pointing out the similarity between the reactivity ratios of different

methacrylates for both GTP and anionic polymerization. In both cases, the ratios are quite different from unity, in contrast to free-radical copolymerizations for which the reactivity ratios do not significantly differ from unity (Table 7-2; Müller, 1990).

Further experimental observations led Quirk and Ren (1992) to propose that GTP occurs solely by the nonreversible dissociative mechanism [Eq. (7-6)]; the key step of which is a rapid complexation of the prop-

**Table 7-1.** Rate constants (in  $1 \text{ mol}^{-1} \text{ s}^{-1}$ ) and activation parameters for the anionic and GTP polymerizations of MMA and *t*BuMA in THF<sup>a</sup>.

		Anionic polymerization			GTP
		Li <sup>+</sup>	Na <sup>+</sup>	Cs <sup>+</sup>	
MMA	$k_p^b$	100	800	860	1250
	$E_a$ (kJ mol <sup>-1</sup> )	24.0	18.3	19.5	16.9
	$\log_{10} A$	7.4	7.0	7.3	6.8
<i>t</i> BuMA	$k_p^b$	6	56	180	800
	$E_a$ (kJ mol <sup>-1</sup> )	32.8	31.2	23.0	19.1
	$\log_{10} A$	8.2	8.7	7.5	7.05
$k_p(t\text{BuMA})/k_p(\text{MMA})$		0.06	0.07	0.21	0.64

<sup>a</sup> Taken from Müller (1990); <sup>b</sup> at  $-40^\circ\text{C}$ .**Table 7-2.** Reactivity ratios for the polymerization of MMA ( $M_1$ ) with other methacrylates ( $M_2$ ) in THF<sup>a</sup>.

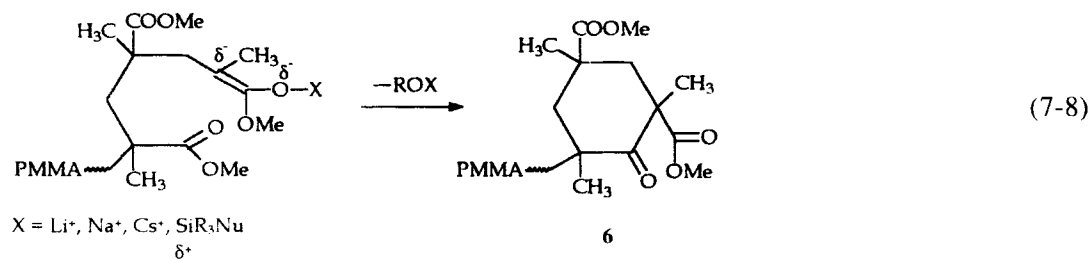
Ester $M_2$	Polym. method <sup>b</sup>	Temp. ( $^\circ\text{C}$ )	$r_1$	$r_2$
Ethyl	GTP (TAS <sup>+</sup> )	20	1.36±0.13	0.51±0.06
	anionic (Na <sup>+</sup> )	-75	1.6	0.8
	radical	60	0.92	1.1
<i>t</i> -Butyl	GTP (TAS <sup>+</sup> )	20	4.59±0.35	0.16±0.06
	anionic (Na <sup>+</sup> )	-69	7.1 ±1.5	0.11±0.07
	radical	60	0.96±0.09	1.3 ±0.19
Decyl	GTP (TAS <sup>+</sup> )	20	1.66±0.14	0.48±0.03
Decyl	anionic (Na <sup>+</sup> )	-90	1.5 ±0.4	0.7 ±0.2
Nonyl	radical	60	1.1	0.9

<sup>a</sup> Taken from Müller (1990); <sup>b</sup> free-radical copolymerization initiated with AIBN in benzene.

agating enolate intermediate with a silyl ketene acetal chain-end function.

- The primary termination reaction in MMA GTP involves a chain-end cyclization reaction to form a cyclohexanone-

type chain end **6**, which is analogous to the termination product of ester enolate anions in corresponding anionic polymerizations [Eq. (7-8)] (Brittain and Dicker, 1989)



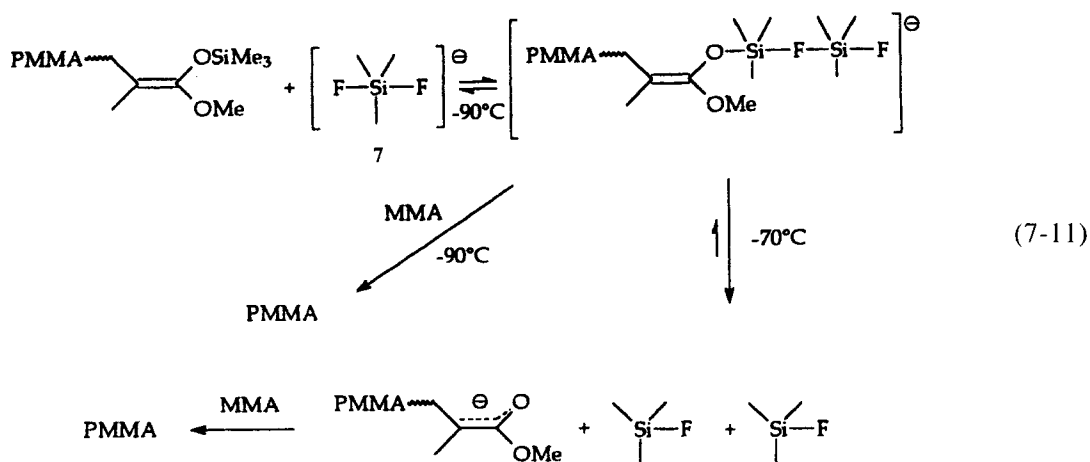
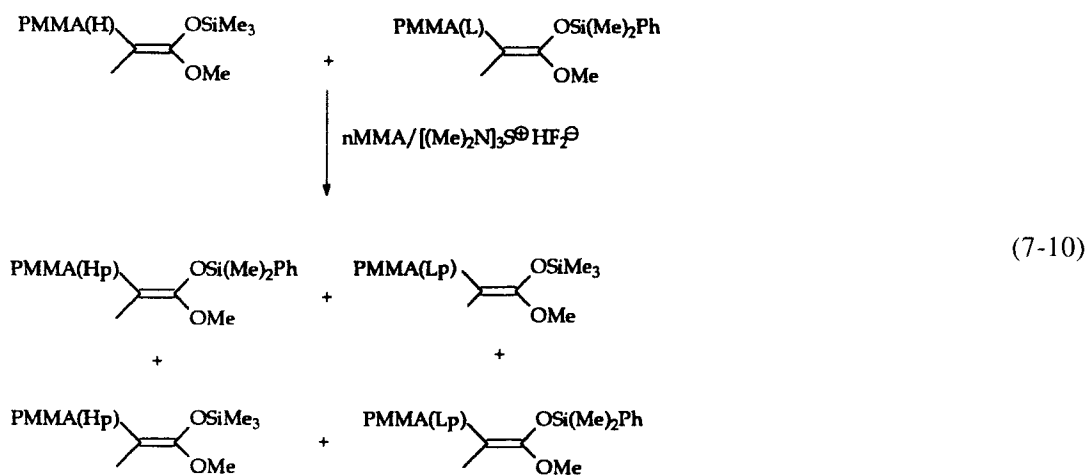
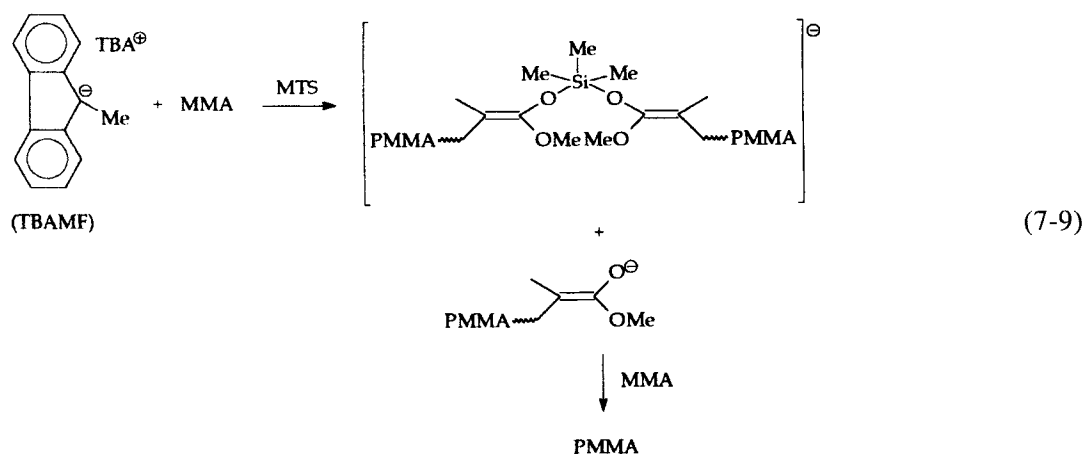
- A chain transfer is observed to carbon acids with  $pK_a$  values in the range 18–25 for MMA GTP (Hertler, 1987).
- Enolate anions can function as the “nucleophilic catalysts” for “anionic” GTP (Quirk and Bidinger, 1989). Indeed, in anionic polymerization of MMA initiated with tetrabutylammonium methylfluorenide (TBAMF), this fluorenide should generate enol groups at the reactive end of the growing chain. However, on the addition of a large excess of MTS to the solution of TBAMF prior to addition of the monomer, the MW was controlled by the MMA to MTS molar ratio rather than by the amount of TBAMF [Eq. (7-9)]. Without the added GTP initiator, only a 14% yield of PMMA was obtained. These results dramatically demonstrate the stabilizing effect of trimethylsilyl ketene acetal, and since PMMA with a quite narrow polydispersity ( $M_w/M_n=1.2$ ) was obtained, the enolate end groups must be in rapid equilibrium with neutral chain ends and thus be available for the monomer addition.
- An unusual negative reaction order (–0.27) kinetic dependence on the silyl ketene acetal end-group concentration (initiator) for GTP polymerization of MMA (Mai and Müller, 1987) and *t*BuMA (Doherty and Müller, 1989) fits the inhibition of the reaction by the initiator and is in agreement with the “dissociative” mechanism.
- In double-labeling experiments, using PMMA of two different molecular weights designed for separation by solubility difference in the two samples, partial exchange has recently been reported by Quirk and Ren (1992). Living PMMA of two distinct molecular weights (H, high MW, and L, low MW), one with trimethylsilyl and the other with a phenyldimethylsilyl end group, were mixed and used to initiate MMA polymerization in

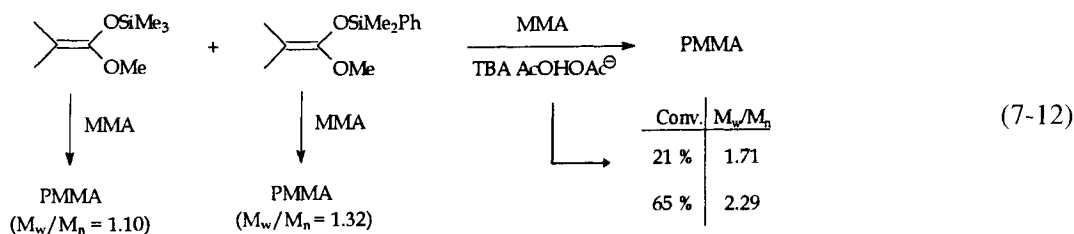
the presence of TASHF<sub>2</sub> as the catalyst [Eq. (7-10)]. Fractionation of the resulting polymeric mixture indicated that exchange of end groups had occurred.

These results provide strong evidence for a dissociative mechanism and appear to somewhat contradict the double-labeling experiments of Sogah and Farnham (1985). Interestingly enough, Webster (1994) has recently pointed out the effect of the polymerization temperature. The double-labeling experiments by Sogah and Farnham were initially conducted at –90 °C [see Eq. (7-7)]. When carried out at –70 °C, some end group scrambling did, however, take place. This observation led Webster to suggest that the quite strong fluoride ion donor, i.e., difluoromethylsiliconate [7 in Eq. (7-11)], reacts with the trimethylsilyl ketene acetal end group leading to two molecules of fluorotrimethylsilane and TAS enolate, in agreement with the reversible dissociative mechanism [Eq. (7-5)]. The small amount of TAS enolate could then catalyze the GTP polymerization by a dissociative mechanism.

Schneider and Dicker (1988) have reported that when catalyzed by oxyanions, such as acetate anions, GTP displayed an enhanced “livingness”, particularly at higher temperature in the presence of a silylated oxyanion, e.g., Me<sub>3</sub>SiOAc. It is interesting to note that the propagation rate is slowed under these conditions, which could appear to be consistent with the reversible dissociative mechanism.

There is evidence for all three of the mechanisms which have been proposed, and the mode of the GTP polymerization more likely depends upon the precise reaction conditions, particularly the nature of the catalyst. As concluded by Webster (1994), “Although all of the data do not quite fit, the evidence weighs heavily on the side of a dis-





sociative process for anion-catalyzed GTP, especially for the strongly nucleophilic systems; for carboxylate-catalyzed GTP, the jury is still out.” Indeed, some evidence for the associative mechanism has recently been found in dual initiator systems (Webster, 1994). Under an associative mechanism with dual initiators, each set of chains would grow at slightly different rates. Therefore the MWD would get broader than when only one initiator is operating. This is the case when dimethylphenylsilyl ketene acetal and trimethylsilylketene acetal were used to polymerize MMA with tetrabutylammonium biacetate as a catalyst [Eq. (7-12)]; the  $M_w/M_n$  increased from 1.71 to 2.29 on increasing the monomer conversion from 20 to 65%.

#### 7.4.2 A Remarkable Macromolecular Architecture

Whatever the issue of the mechanistic discussions, GTP has provided the polymer chemist with a synthetic tool that is versatile and tunable for macromolecular engineering.

As in other living polymerizations, the MW of the poly(meth)acrylates obtained by GTP is determined by the monomer-to-initiator molar ratio. Although MW can easily be controlled in the 1000–20 000 range, higher molecular weights are difficult to obtain. However, the major advantage over classical anionic living polymerizations is the possibility of operating at (and above) ambient temperature, at least for the meth-

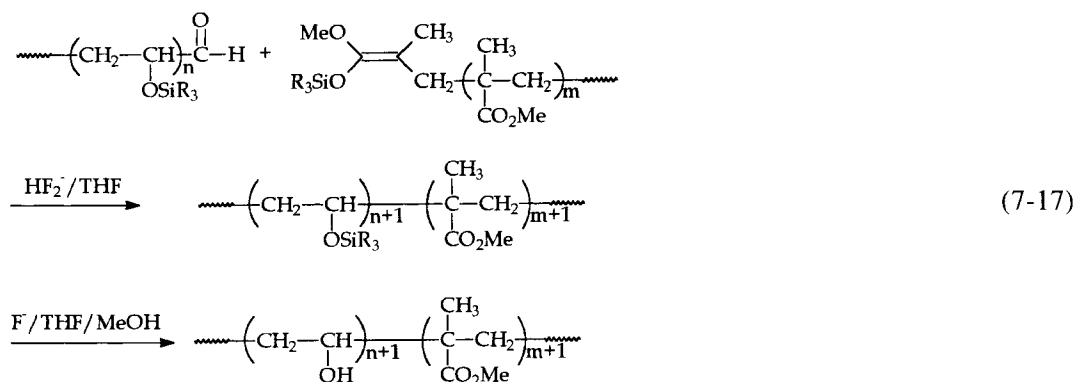
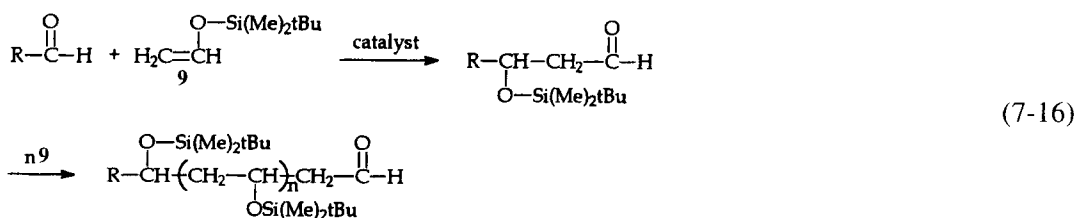
acrylic esters. From the technology point of view, this solves in the same way the crucial problem of heat transfer in fast and exothermic reactions (a dramatic drawback often encountered in the polymerization of methacrylic esters). Even though most activity has concentrated on (meth)acrylates, other polar monomers, e.g., acrylonitrile and *N,N*-dimethylacrylamide, have also been polymerized by GTP (Sogah et al., 1987).

Random copolymers have been synthesized by adding a mixture of monomers of the same family, either all methacrylate or all acrylate, to the initiator and catalyst (Webster et al., 1983). The large difference in reactivity between the various acrylic monomers prevents random group transfer copolymerization of their mixtures. Similarly block copolymers within the same family form easily. An AB block copolymer with methacrylate and acrylate segments is prepared by polymerizing the less reactive methacrylate monomer first and then adding the acrylate monomer. An ABA triblock copolymer where A=PMMA and B=poly-caprolactone (PCL) has been readily synthesized by the addition of two equivalents of trimethylsilylcyanoide to  $\alpha,\omega$ -diacrylo PCL, which produced a macroinitiator in situ. Upon the addition of MMA, rapid polymerization occurs at both chain ends (Sogah et al., 1984).

Also,  $\alpha$ - and  $\alpha,\omega$ -functional (telechelic) polymers, including poly(meth)acrylate macromonomers, have been prepared by GTP (Sogah and Webster, 1983). The functional-







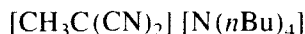
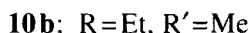
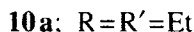
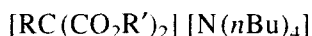
cess of silyl vinyl ether **9** to an aldehyde as initiator gave a silylated vinyl alcohol polymer with a terminal aldehyde group [Eq. (7-16)], the MW of which was controlled by the molar ratio of the silyl vinyl ether to the aldehyde initiator. The best control of molecular weight was obtained with *tert*-butyldimethyl silyl vinyl ether over a wide temperature range ( $-80$  to  $+70^\circ\text{C}$ ).

Unlike the GTP of methacrylic esters in which the silyl group is transferred from the initiator to the monomer, the polymerization of silyl vinyl ethers, referred to as aldol-GTP, involves transfer of the silyl group from monomer to initiator. A catalyst (ca.  $10^{-3}$  mol% relative to monomer) is required for the process to occur. Although Lewis acids such as diisobutylaluminum chloride and titanium tetrachloride are effective as catalysts, the preferred catalysts are zinc halides. In contrast to the GTP of MMA, anionic catalysts, particularly fluoride sources, are less efficient for the aldol-GTP than Lewis acids. Anionic catalysts are actually

known to strongly coordinate not only to the incoming silyl vinyl ether, but also to the backbone siloxy groups. Besides aldehydes, electrophiles such as benzylhalides and acetals can also be used as initiators. Interestingly enough, diblock copolymers of silylated vinyl alcohol and MMA were synthesized by treatment of the aldehyde-terminated polymer with living PMMA made by GTP [Eq. (7-17)]. Upon cleavage of the silyl groups with fluoride ions in the presence of methanol, a copolymer containing hydroxyl groups was obtained, the degree of hydrophilicity of which was tuned by varying the size of the PVA blocks.

## 7.5 Metal-Free Anionic Polymerization

Reetz (1988) has explored the possibility of employing metal-free carbon nucleophiles as initiators in the anionic polymerization of acrylates. By using the resonance-



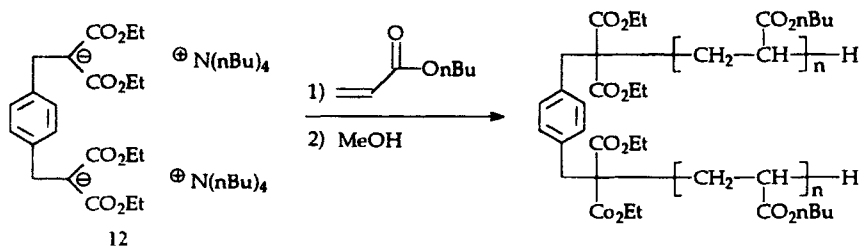
stabilized initiators **10** and **11** with the non-metallic tetrabutylammonium counterion, *n*-butyl acrylate was polymerized almost quantitatively at room temperature both in THF and toluene.

Good control of the MW up to at least 20 000 and a narrow  $M_w/M_n$  of ca. 1.3 were reported. Similarly, the dianion **12** also proved to be an effective initiator in the polymerization of *n*BuA [Eq. (7-18)]. More recently, Sivaram et al. (1991) reported on the controlled polymerization of methyl acrylate as initiated by the functional carbanionic initiator **13** at ambient temperature in THF. Methyl acrylate oligomers ( $M_n < 5000$ ) with reactive chain ends, i.e., bearing oxazoline groups, have accordingly been synthesized.

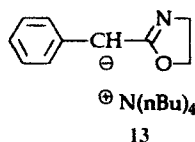
Although these preliminary results provide very exciting prospects for the living polymerization of acrylate monomers, it is

still difficult at present to explain why the ammonium carbanions are such excellent initiators at room temperature. Reetz (1988) has suggested that the positive charge is not localized on the nitrogen atom, but rather on the four  $\alpha$ -carbon atoms, leading to a tetrahedral distribution of charge. The acrylic monomer may approach one corner of the tetrahedron in such a way that a kind of solvation may be seen. Larger tetraoctylammonium did not allow controlled polymerizations, leading to polyacrylates with broad MWD. The long substituents pointing from the tetrahedral position probably prevent a tight and ordered transition state. Further experimental data, including the tacticity of the polymers, would be enlightening.

The much more stable  $\text{P}_4^+$  ion, i.e.,  $\{[(\text{Me}_2\text{N})_3\text{P}-\text{N}]_3\text{P}-\text{NH}'\text{Bu}\}^+$ , may be a better gegenion than the tetrabutylammonium counterion.  $\text{P}_4^+$  ester enolate polymerized MMA at 60°C to give a very low molecular weight distribution ( $M_w/M_n=1.1$ ) (Pietzonka and Seebach, 1993). Unlike other anionic polymerization processes, this one did not work well at low temperature. At -78°C, a polydispersity of 2.3 was observed. Very recently, Hogen-Esch and co-



(7-18)

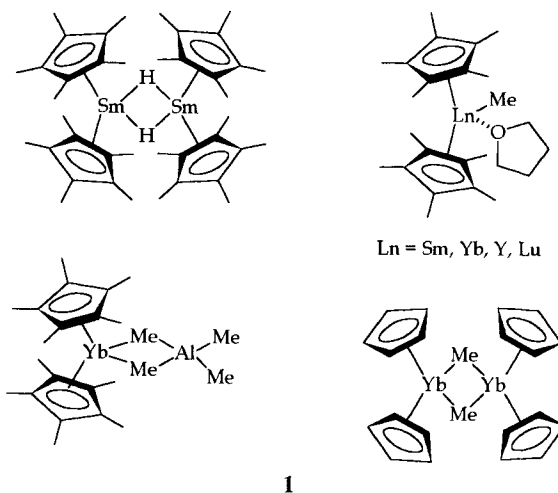


workers found that the polymerization of MMA in THF at ambient temperature was living ( $M_w/M_n < 1.2$ ) when initiated by  $\text{Ph}_3\text{C}^-$ ,  $^+\text{PPh}_4$  (Dimov et al., 1996; Zagala and Hogen-Esch, 1996). In contrast, the polymerization of *n*BuA under identical conditions was not under control. Polymer yields, although high, were not quantitative, and the polydispersities were broader and the initiator efficiencies were higher than unity. Interestingly enough, multinuclear NMR studies indicated the presence of phosphorylides in these polymerizations, formed by the addition of the PMMA enolate anion to one of the phenyls of the  $^+\text{PPh}_4$  (Baskaran et al., 1997). Furthermore, the kinetics of MMA polymerization were consistent with the presence of a small fraction of a highly reactive phosphonium enolate in equilibrium with the unreactive, or the much less reactive, ylide (Baskaran and Müller, 1997). The fact that the MWD of the PMMA prepared in the presence of  $^+\text{PPh}_4$  is quite narrow ( $M_w/M_n < 1.2$ ) suggested that equilibrium between the phosphonium enolate and the ylide is rapid on the polymerization time scale. So far, this is the first example of an ylide-mediated vinyl polymerization. The precise role of the ylides in these polymerizations remains to be elucidated.

## 7.6 Nucleophilic/Coordinative Polymerization

### 7.6.1 Organolanthanides (III)-Initiated Polymerization

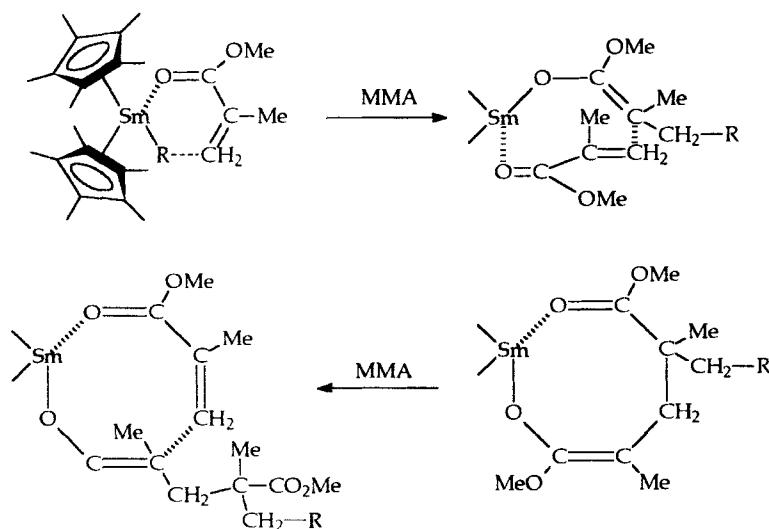
The organolanthanide (III) complexes were the first initiators found to cause living polymerization of MMA, leading to PMMA chains of very high MW ( $M_n > 5 \times 10^5$ ) with extremely narrow MWD ( $M_w/M_n < 1.05$ ) (Yasuda et al., 1992, 1993). Organolanthanides used by Yasuda include lanthanide



hydrides, trialkylaluminum complexes of alkylanthanides, and simple alkyl complexes that were synthesized starting with  $\text{Ln}(\text{C}_5\text{Me}_5)_2\text{Cl}$ .

The polymerization proceeded over a wide range of temperature from  $-95$  to  $60^\circ\text{C}$ . Syndiotacticity exceeding 95% was observed when the polymerization was conducted in THF or toluene at the lower temperatures. The apparent rate of polymerization was found to increase on increasing the ionic radius of the metal ( $\text{Sm} > \text{Y} > \text{Yb} > \text{Lu}$ ) and to decrease on increasing the steric bulkiness of the auxiliary ligands ( $\text{C}_5\text{H}_5 > \text{C}_5\text{Me}_5$ ) (Yasuda and Ihara, 1995).

Yasuda et al. (1992) have isolated the 1:2 adduct of  $[(\text{C}_5\text{Me}_5)_2\text{SmH}]_2$  and MMA, and determined its structure by single crystal X-ray analysis. One of the MMA units is linked to the metal in its enolate form, while at the other end the second (penultimate) MMA unit is coordinated to the metal by its carbonyl group. Therefore, in the initiation step, the hydride is expected to attack the  $\text{CH}_2$  group of MMA, generating a transient  $\text{Sm-OC}(\text{OCH}_3)=\text{C}(\text{CH}_3)_2$  species. Then the next incoming MMA molecule could participate in a nucleophilic 1,4-addition to afford an eight-membered cyclic intermediate [Eq. (7-19)]



(7-19)

On the basis of the X-ray structural data and of the mode of polymerization, Yasuda described these organolanthanide initiated polymerizations as occurring owing to a “coordinated anionic mechanism with an 8-membered transition state.” The observed unique initiator could primarily originate from the large ionic radii [1.0–1.1 Å (0.1–0.11 nm)] of the rare earth metals compared to those of Li, Mg, and Al [0.68–0.73 Å (0.068–0.073 nm)], in addition to their sufficiently small electronegativity (1.1–1.2).

Chiral organolanthanides have also been used in the stereoregular polymerization of MMA. Isotactic ( $\geq 90\%$ ) polymerization of MMA was achieved using  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_5)\text{C}_5\text{Me}_4\text{-1S,2S,5R-neomenthyl-LnR}$  with  $\text{R}=\text{CH}(\text{SiMe}_3)_2$  or  $\text{N}(\text{SiMe}_3)_2$ ; while  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_5)\text{C}_5\text{H}_4\text{-1S,2S,5R-menthyl-LnR}$  [ $\text{Ln}=\text{Lu, Sm}$ ;  $\text{R}=\text{CH}(\text{SiMe}_3)_2$  or  $\text{N}(\text{SiMe}_3)_2$ ] produced syndiotactic PMMA (ca. 70%) (Yasuda and Ihara, 1995). The molecular weight control is very poor and  $M_w/M_n$  is as broad as 15, even with bimodal distributions. Nevertheless, this is the first example of polymer stereochemistry con-

trol by altering the chirality of a metal-based ligand.

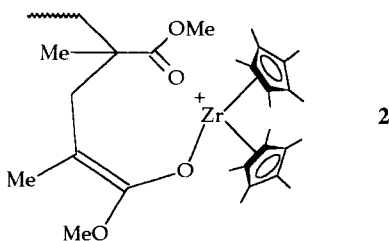
Yasuda also disclosed the efficient initiating properties of  $\text{SmMe}(\text{C}_5\text{Me}_5)_2$  (THF) and of  $\text{YMe}(\text{C}_5\text{Me}_5)_2$  (THF) in the living polymerization of acrylic esters, i.e., methyl acrylate (MeA), ethyl acrylate (EtA), and butylacrylate (*n*BuA), although these reactions are nonstereospecific (Yasuda and Ihara, 1995). Again,  $M_w/M_n$  is extremely narrow, i.e.,  $<1.05$ , even for polyacrylates of  $M_n=4\times 10^5$ . The rate of polymerization increases with increasing bulkiness of the alkyl acrylates. In the case of MeA, the polymerization in toluene at  $0^\circ\text{C}$  is complete in 300 s, the  $M_n$  and conversion increasing with polymerization time, whereas the polymerization is complete in 5 s for the polymerization of EtA and *n*BuA.

Random and block copolymers of alkylacrylates and MMA have been synthesized in a perfectly controlled way. A typical example is provided by the ABA type triblock copolymerization of MMA/*n*BuA/MMA, as initiated by  $\text{SmMe}(\text{C}_5\text{Me}_5)_2$  (THF) in toluene at  $0^\circ\text{C}$ . The resulting triblock copolymers  $\text{P}(\text{MMA-}b\text{-}n\text{BuA-}b\text{-MMA})$ , of

$M_n > 100\,000$  with  $M_w/M_n < 1.1$ , exhibited interesting thermoplastic elastomer properties (Yasuda and Ihara, 1995).

It is also worth mentioning that rare earth metal initiated polymerizations of lactones such as  $\epsilon$ -caprolactone,  $\delta$ -valerolactone, and  $\beta$ -propiolactone again produce high MW polyesters with narrow MWD. Block copolymerizations of such lactones and MMA proceed smoothly to give copolymers with  $M_w/M_n = 1.10$ – $1.25$ . Similar organolanthanide (III) complexes were found to display excellent catalytic behavior towards polymerization of olefins and  $\alpha$ -olefins, including their copolymerization with polar monomers such as (meth)acrylates and lactones. Finally, more complex systems like  $\text{Ln}(\text{acac})_3/\text{AlR}_3/\text{H}_2\text{O}$  also exhibit good activity towards the polymerization of oxiranes. All these extremely interesting homo- and copolymers have been reviewed very recently by Yasuda and Ihara (1995).

It is interesting to point out the work by Collins and Ward (1992), in which the MMA polymerization is initiated in  $\text{CH}_2\text{Cl}_2$  by cationic zirconocene compounds such as  $[\text{Zr}(\text{C}_5\text{Me}_5)_2\text{Me}(\text{THF})]^+(\text{BPh}_4)^-$ . A mechanism involving an eight-ring intermediate, analogous to that described by Yasuda, has also been proposed.

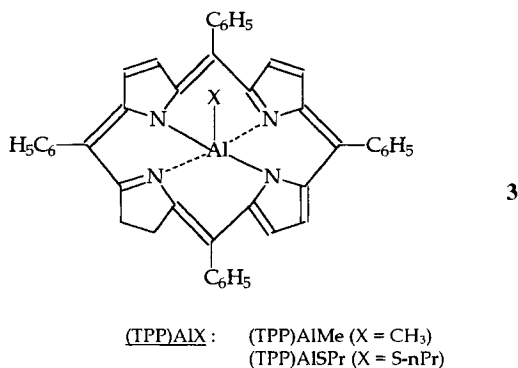


In the presence of a proton source, this cationic complex is able to polymerize MMA up to high monomer conversion. However, the molecular weight distributions are broader than those obtained by in-

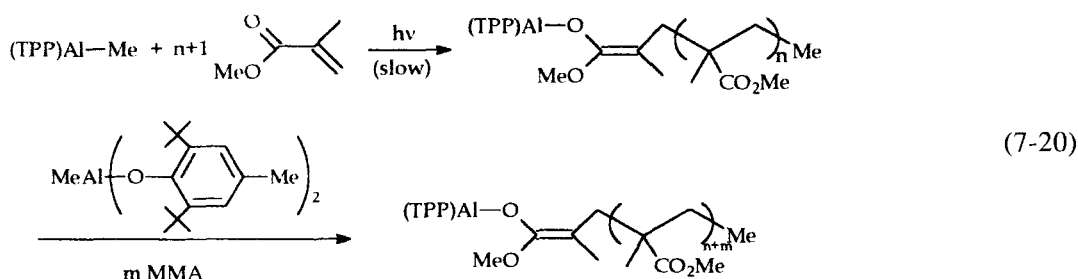
itiation with organolanthanide complexes, but still in the range  $M_w/M_n = 1.2$ – $1.4$ . The polymerization of *n*BuA was also studied and poly(*n*-butyl acrylate) could be prepared in high yield at low temperature with narrow MWD, e.g.,  $M_w/M_n$  of ca. 1.25 at  $-78^\circ\text{C}$ . This polymerization was not living and the principal termination process involved back-biting cyclization, as revealed by MALDI–TOF mass spectra of low MW polymer. At higher temperatures, the growing chains were deactivated by this process and also by competitive  $\alpha$ -hydrogen transfer, such that high monomer conversions were not obtained (Li et al., 1997).

### 7.6.2 Metalloporphyrin-Mediated Nucleophilic Polymerizations

Both methacrylates and acrylates are readily polymerized by tetraphenylporphyrinatoaluminum derivatives having the following structures



Initially, the MMA polymerization was initiated by the methyl-substituted aluminumporphyrin (TPP)AlMe (Kuroki et al., 1987; Hosakawa et al., 1991). The polymerization was living at room temperature, leading to perfect control of every molecular parameter. As a typical example, block copolymers of MMA with propylene oxide could easily be synthesized (Kuroki et al., 1988). How-

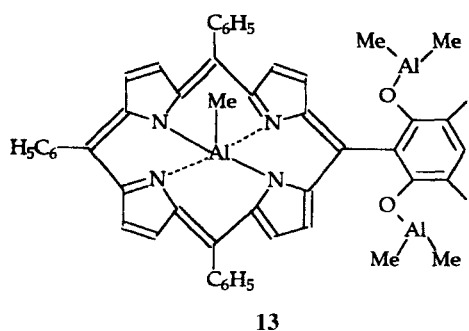


ever, the polymerization that required irradiation by visible light was slow, so only 6% of monomer conversion was reached within 2.5 h in  $\text{CH}_2\text{Cl}_2$  at  $35^\circ\text{C}$ . The mechanism proposed by Inoue is basically based on nucleophilic reactions involving an ester enolate as the growing active species [Eq. (7-20)].

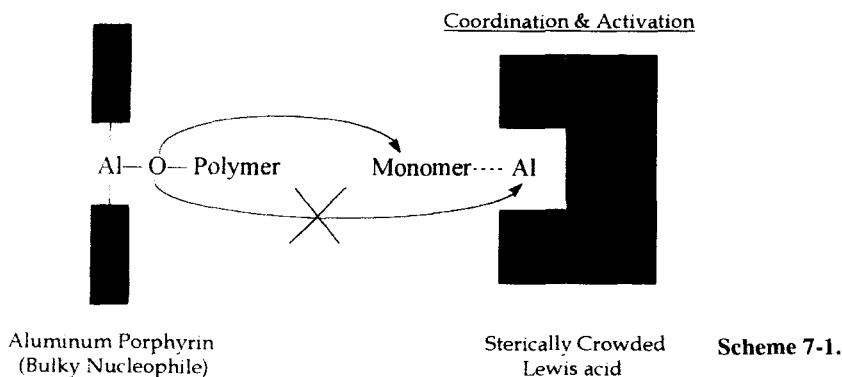
It was anticipated that activation of the monomer by a judiciously chosen Lewis acid should enhance its reaction with the porphyrin “catalyst” provided that the chosen acid does not polymerize the monomer (Scheme 7-1).

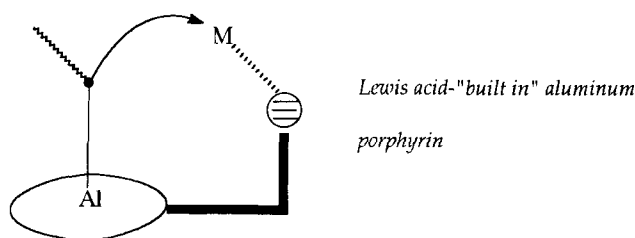
This condition is fulfilled by the use of bulky aluminum phenoxides (Kuroki et al., 1991), the addition of which to (TPP)AlMe and MMA is reported to trigger a 45 000-fold acceleration of the polymerization so that narrow MWD ( $M_w/M_n < 1.07$ ) PMMA chains are quantitatively formed in less than 3 s at  $35^\circ\text{C}$  [see Eq. (7-20)]. When less bulky aluminum alkyls were used, e.g.,  $\text{Me}_3\text{Al}$ ,  $\text{Et}_3\text{Al}$ , no acceleration took place.

In order to extend the concept of the so-called “high-speed anionic living polymerization” obtained by the combination of a metalloporphyrin initiator and a bulky Lewis acid catalyst, Inoue et al. (1995) designed a novel type of initiator carrying a nucleophilic site and a Lewis acidic site in one molecule of porphyrin **13**.



The strategy is to bind a Lewis acidic site for monomer activation covalently to the rigid skeleton of a porphyrin, so that the site



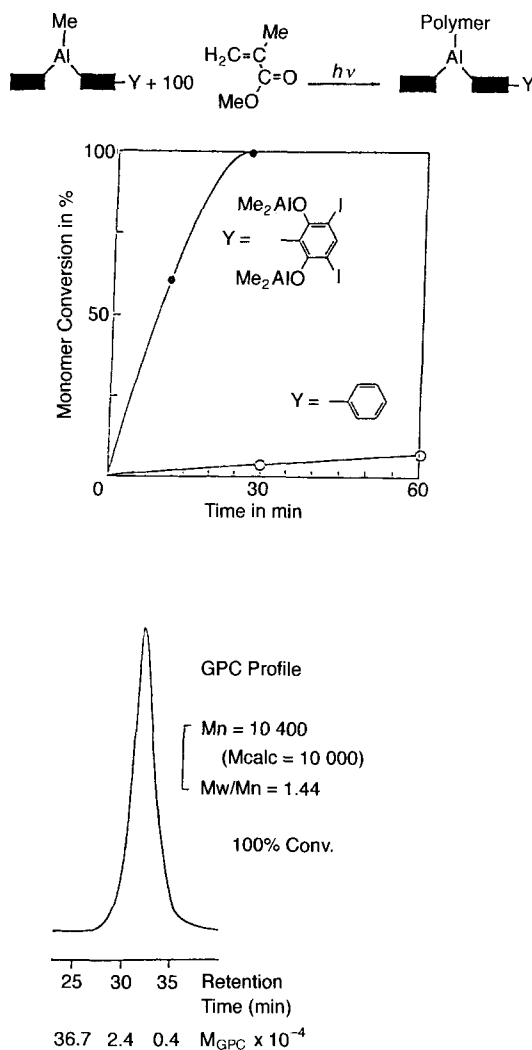


Scheme 7-2.

for monomer activation is located at an appropriate distance and steric position for them to cooperate with each other (Scheme 7-2).

The monomer activation by the intramolecular Lewis acid site is illustrated by the MMA polymerization with **13** as initiator in  $\text{CH}_2\text{Cl}_2$  at room temperature (Fig. 7-1).

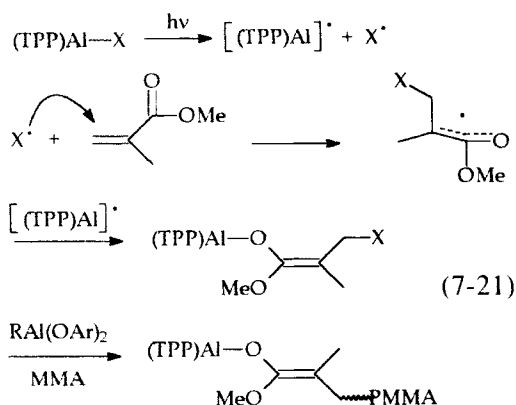
It is worthwhile noting the synthesis of ultra-high molecular weight ( $>1 \times 10^6$ ) PMMA with narrow polydispersity ( $M_w/M_n=1.2$ ) (Adachi et al., 1992). Acrylates have also been polymerized successfully, as illustrated by the synthesis of *PtBuA* with a narrow MWD ( $M_w/M_n$  of ca. 1.1). Less bulky acrylates, e.g., ethyl and isobutyl acrylates, require a lower polymerization temperature ( $-70^\circ\text{C}$ ), but, even at this temperature, side termination reactions could not be avoided, as illustrated by the broader polydispersity ( $M_w/M_n=1.2-1.4$ ). (TPP) AISP<sub>r</sub> has recently proved very efficient at promoting the MMA polymerization in the dark (Adachi et al., 1993). At  $35^\circ\text{C}$ , this porphinatoaluminum thiolate polymerizes MMA quantitatively within 18 h to give a polymer of  $M_n=22\,000$  with an  $M_w/M_n$  of 1.12. Again, the addition of a bulky Lewis acid leads to complete conversion within a couple of minutes. The fact that the MMA polymerization does not require irradiation when initiated by (TPP)AISP<sub>r</sub> has been initially accounted for by the highly nucleophilic nature of the thiolate aluminum porphyrins. However, Davis et al. (1994) have also proposed that the initiation step could occur by a bond homolysis followed by a radical at-



**Figure 7-1.** Time-conversion profile for the MMA polymerization as initiated by **13** ( $[\text{MMA}]_0/[\mathbf{13}]_0=100$ ) in  $\text{CH}_2\text{Cl}_2$  at room temperature [from Inoue et al. (1995), with the permission of Hüthig & Wepf Publishers, Zug, Switzerland].

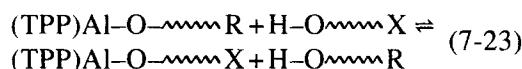
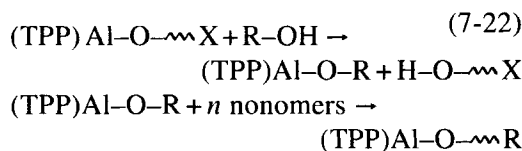


tack on the methacrylate, and further by coordination of the formed end radical with the TPP-Al radical to yield the propagating species [Eq. (7-21)]. Comparatively, Reddy et al. (1993) reported that methylaluminumoxane forms a weak complex with MMA so that, on exposure to UV radiation, it polymerizes to high conversion. The process exhibits a living behavior, although the  $M_w/M_n$  or 1.5–1.7 suggests the occurrence of side termination and/or transfer reactions. The authors claimed that the active species are free radicals, which are stabilized by methylaluminumoxane.



It has also been demonstrated by Inoue that (TPP)Al-X derivatives are very efficient and versatile initiators for the living ring-opening polymerization of lactones, lactides, and epoxides ( $\text{X}=\text{OR}$ ,  $\text{Cl}$ ,  $\text{O}_2\text{CR}$ ) (Inoue et al., 1990; Inoue and Aida, 1993). The addition of alcohols to the lactones or epoxides polymerizing solution does not terminate the polymerization. Alcohols act in this system as chain-transfer agents [Eq. (7-22)]. The inability of alcohols to terminate the polymerization led Inoue to coin the term “immortal polymerization”. The most remarkable feature of the proposed process arises from the rapid exchange between the growing polymers attached to the (TPP)Al moiety and the dead ones possessing the OH end group [Eq. (7-23)]. The exchange seems

to be much faster than the propagation, hence the MWD of the resulting polymers remains narrow, in spite of the chain transfer. Note that no data are available concerning a possible extension of this “immortal polymerization” to (meth)acrylates.



Very recently, the accelerated living polymerization of methacrylonitrile with aluminum porphyrin initiators has been achieved by the selective activation of the growing species. Whereas the monomer was previously activated by bulky Lewis acids, the propagating sites activation involves less-hindered Lewis bases such as pyridine, triphenyl phosphine, or 1-methylimidazol (Sugimoto et al., 1996). This strategy has allowed for the controlled synthesis of P (MMA-*b*-methacrylonitrile) diblock copolymers.

## 7.7 “Ligated” Anionic Polymerization

If the goals of general and practical macromolecular engineering of poly(meth)acrylic esters are considered, a number of important requirements should be met, such as: living, high MW homo- and copolymerization processes compatible with “classical” monomers such as styrenes, dienes, vinyls, and oxiranes; stereoselectivity, particularly for PMMA (over 80% syndiotacticity); and in different solvents, preferably in hydrocarbons (and possibly avoiding THF).

If the wish is now rightly to implement (co)polymerization processes where these

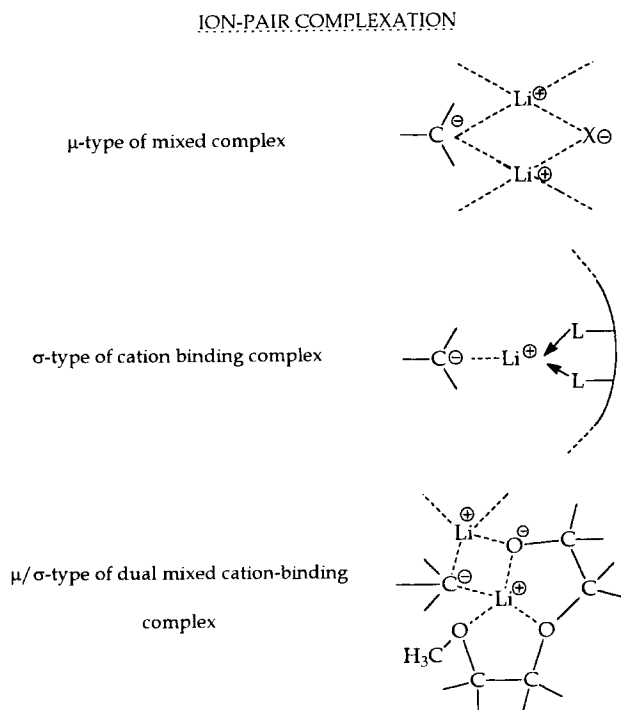
goals would be achieved all together, it has to be admitted that, despite their real merits, none of the first three strategies mentioned above meets that demanding challenge. This is the reason why the last aspect involving ligated anionic species, which in principle appeared able to be answered, has been thoroughly revisited, in depth, and significantly improved to a point where the above-described prospects have mostly been implemented.

The basic idea of a ligand-modified or "ligated" anionic polymerization (LAP) is to use a suitable ligand (or ligands) to interact coordinatively with a very active metal containing (usually alkali metals) initiating and/or propagating ion-pairs; in this situation, these ligands fulfill a variety of functions:

- 1) modulation of the electron density at the metal enolate ion-pair and, therefore, of its stability and reactivity;
- 2) provision of a steric basic barrier blocking a large enough space area around the metal containing ion-pairs, and thus possibly minimizing the extent of secondary reactions;
- 3) promotion of new complexation equilibria displacing classical equilibria between different ion-pairs and/or aggregates, hopefully leading to the existence of a unique active species.

### 7.7.1 Ion-Pairs Complexation: Nature of Ligands

Coordination chemistry offers us two different families of ligands able to modify both the electronic distribution and the steric hindrance around the ion-pair: the so-called  $\mu$ -(four-center delocalized) and  $\sigma$ -(simple dative bonds) complexes (Scheme 7-3; for clarity, carbanions are represented rather than the enolate anions). Several examples of the first type appeared during the last two



Scheme 7-3.

decades, e.g., the Al-alkyls of Hatada et al. (1986), the alkyl metal alkoxides of Lochmann and co-workers, (Lochmann and Trekoval, 1979; Lochmann et al., 1992; Vleck, 1990), and the Al-phenoxides of Ballard et al. (1992).

Teyssié and his co-workers have proposed the use of LiCl for lithium alkyl-initiated polymerization, a somewhat more efficient combination (Varshney et al., 1990a, 1990b). Multinuclear NMR spectroscopy has shown the formation of a stable trinuclear  $\mu$ -type complex, which contains two LiCl per enolate active site (Wang et al., 1993a, 1994a, 1995a). Thus the  $\mu$ -type of complexation between lithium enolate and LiCl (or LiOtBu) benefits from strong spontaneous electrostatic interactions, all cations in the system being associated with enolate oxygen (and probably carbanion as well), while also in close contact with the ligand ions. Accordingly, the self-associative O-Li bond in lithium ester enolates can be completely perturbed, resulting in a rearranged tight and highly charged delocalized  $\mu$ -complex. Undoubtedly, this is an important feature in stabilizing the formed active complex (Teyssié et al., 1990) at the origin of living polymerizations, as promoted by LiX (X=halogen, OtBu) but also by simple  $R_3Al$  ligands (Hatada et al., 1986).

For instance, LiCl (five molar excess with respect to the lithium active sites) is a very practical and efficient ligand to work in moderately polar solvent (pure THF or its mixtures with hydrocarbons) at a low polymerization temperature LiCl promotes the perfectly living homo- and block (two-directional) (co)polymerization of MMA and *tert*-butylacrylate (*t*BuA) in THF at  $-78^\circ\text{C}$ . However, the anionic copolymerization of MMA/*t*BuA mixtures under the same conditions always leads to very poor results (Jacobs et al., 1990). In other words, the chlorine ligand is not bulky enough to block a

given space area around the  $\mu$ -type complex in order to avoid the attack of the very active complex on the small methoxy group of the MMA antipenultimate unit in the polymer chain (see also Sec. 7.7.2.2).

Playing on that concept of the ligand structural characteristics, Teyssié could first demonstrate that in nonpolar (hydrocarbon) media, an hindered chelating  $\sigma$ -ligand, i.e., dibenzo-18-crown-6-ether (DB18CE6) with a sodium cation, was a better alternative to control a number of problems such as higher temperature (up to  $5^\circ\text{C}$ ), random copolymerization, etc. (Varshney et al., 1992). Nevertheless, the  $\sigma$ -type of lithium cation-binding ligands studied, i.e., HMPA, DME, and substituted or unsubstituted crown ethers, were still not powerful enough to destroy the self-aggregation of lithium ester enolates (Wang et al., 1994a). This is probably due to the presence of relatively strong O-Li associative bonds in lithium ester enolates leading to a coexistence of ligand-free and -added species (see also Sec. 7.7.2.1).

It was hence a logical step to combine both concepts and use a family of  $\mu/\sigma$  dual ligands, the best example as yet (Bayard et al., 1994) being lithium 2-(2-methoxyethoxy)ethoxide (LiOE<sub>2</sub>M). A first multinuclear NMR spectroscopic characterization (Wang et al., 1994b) of complexation between LiOE<sub>2</sub>M and a lithium ester enolate, i.e., methyl  $\alpha$ -lithioisobutyrate (MIBLi), indicated that such a  $\mu/\sigma$  dual ligand is exceptionally effective by reacting with highly aggregated lithium enolate through a " $\mu$ -mixed/ $\sigma$ -binding" pathway, with the formation of a bulky and relatively large charge-separated  $\mu/\sigma$  complex of the type sketched in Scheme 7-3.

The new " $\mu/\sigma$ -ligated anionic initiators" are remarkably efficient at controlling living, high MW polymerizations of acrylic esters, including primary ones down to butyl,

as well as their block and random copolymerization and end-group functionalization at moderately low temperatures; all of which can be done in hydrocarbon media (a definite advantage over THF for process scaling-up) while maintaining a high (ca. 80%) syndiotacticity (PMMA displacing a 130 °C  $T_g$ ) (Wang et al., 1995a, 1995b).

## 7.7.2 Effect of Ligands on Thermodynamics

### 7.7.2.1 Coordination Strength of $\sigma$ -Chelating Ligands

The lack of a sufficient coordination strength of crown ethers towards lithium ester enolates, particularly of 12CE14, i.e., one of the most specific  $\sigma$ -coordinating ligands for the lithium cation (Power, 1988), is directly reflected in their very low efficiency at promoting the anionic living polymerization of (meth)acrylates (Table 7-3). Nevertheless, substitution of the sodium cation for the lithium cation in several crown ether-Mt<sup>+</sup> complexed initiator pairs greatly improved the situation (Varshney et al., 1992). A perfectly living polymerization of MMA can indeed be achieved even at 5 °C in toluene, as long as the CEs are sterically

hindered. Along the same lines, the K211-Li<sup>+</sup> pair was also found to work efficiently by inducing a very narrow polydispersity of living PMMA in THF at -78 °C (Johann and Müller, 1981; Wang et al., 1994a). However, no control was observed when the *n*-butylacrylate (*n*BuA) was polymerized at -78 °C in the presence of various types of cryptands (Table 7-3).

These results pave the way for two promising approaches to successful  $\sigma$ -ligation in relation of the process "livingness":

- 1) enhancing the coordination of the complexing agent versus lithium atoms by using an even more powerful ligand (e.g., K211),
- 2) reducing the associative strength of the O-Mt bond in the metal enolate by increasing the size of the associated cations.

### 7.7.2.2 Steric Hindrance Around the "Ligated" Ion-Pairs

As remarked in Sec. 7.7.1,  $\mu$ -type ligands exhibit a high propensity to coordinate with lithium enolate ion pairs, in sharp contrast to the complexation with crown ethers. Accordingly, an increase in the steric hindrance

**Table 7-3.** Anionic polymerization of alkyl(meth)acrylates initiated with complexed (diphenylmethyl)lithium (I). ( $[I]_0 = 4.0 \times 10^{-4}$  mol l<sup>-1</sup>).

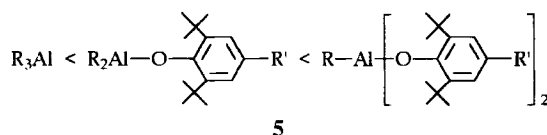
Monomer	Ligand (L) <sup>b</sup>	THF: toluene (v/v)	Temp. (°C)	Time (min.)	Yield (wt.%)	$M_{nSEC}$ ( $\times 10^{-3}$ )	$M_w/M_n$	Initiator efficiency
MMA	12-crown-4	5:95	-78	30	72		— <sup>d</sup>	
	12-crown-4	100:0	-20	60	85	64.0	1.20	0.38
	12-crown-4	5:95	-20	30	60		— <sup>d</sup>	
	15-crown-5	100:0	-20	5	95	23.0	4.50	0.55
	18-crown-6	100:0	-20	5	90	14.0	3.50	0.45
<i>n</i> BuA	12-crown-4	5:95	-78	120	12		— <sup>d</sup>	
	K211 <sup>c</sup>	100:0	-78	120	0			
	K211 <sup>c</sup>	0:100	-78	120	16			

<sup>a</sup> Taken from Wang et al. (1995a); <sup>b</sup>  $[L]_0/[I]_0 = 2$ ; <sup>c</sup> K211 cryptand ( $[I]_0 = 2.0 \times 10^{-4}$  mol l<sup>-1</sup>); <sup>d</sup> multimodal MWD.

around the formed stable complex, whatever its origin, brings about a significant improvement of the "livingness" of the polymerization under more demanding conditions. Such a steric hindrance effect around the active complex is strongly supported by numerous examples:

- 1) The so-called "screened" anionic polymerization (SAP) (Davis et al., 1994) provides unequivocal proof of the important steric influence on the living process of the bulky substituents, e.g., 2,6-*tert*-butyl substituted phenoxy, in an alkyl-aluminum based  $\mu$ -type ligand. For instance, the controlled synthesis of highly syndiotactic PMMA can be promoted by a *t*-BuLi, aluminum alkyl/phenoxide initiator system in toluene solution. Interestingly enough, the upper temperature at

which the living character of the MMA polymerization is preserved increases from  $-78$  to  $0^\circ\text{C}$  and even  $40^\circ\text{C}$  in the following sequence (Wang et al., 1995 a).



with  $\text{R}=\text{Me}, \text{Et}, i\text{Bu}$  and  $\text{R}'=\text{H}, \text{Me}, t\text{Bu}$ .

- 2) The living character of the 2-ethylhexyl acrylate (2EtHA) under the conditions given in Table (7-4) dramatically decreases with a diminishing steric barrier of the X moiety around the formed  $\text{LiX}-\text{LiR}$  complex,  $\text{Me}_2\text{O}^- > t\text{BuO}^- > \text{Cl}^-$ .
- 3) As illustrated in Table (7-5), the very sensitive random copolymerization of MMA-

**Table 7-4.** Anionic polymerization of 2-ethylhexyl acrylate in 9:1 (v/v) toluene-THF using the  $\text{LiX}-\text{RLi}$  initiator system<sup>a</sup>.

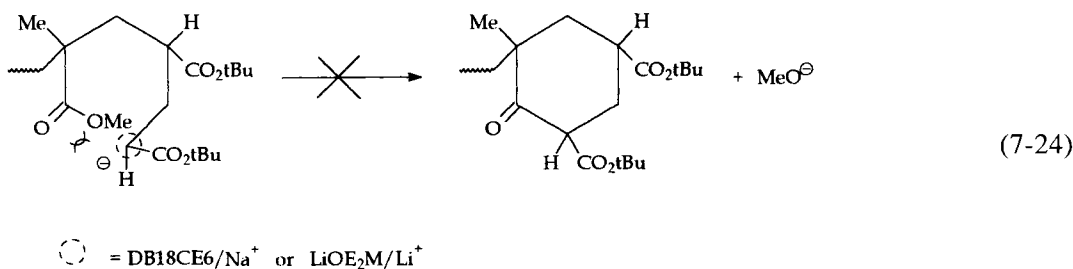
$\text{LiX/RLi}$ (mol/mol)	Temp. ( $^\circ\text{C}$ )	Time (min)	Yield (wt. %)	$M_{\text{thcal}}$ ( $\times 10^{-3}$ )	$M_{\text{nsfc}}$ ( $\times 10^{-3}$ )	$M_w/M_n$	Living character
$\text{LiCl/DPMLi}$ (5:1)	$-78$	60	25	5.0	17.5	2.50	no
$\text{LiOtBu}/t\text{BtBLi}$ (3:1)	$-60$	2	100	9.2	16.6	1.09	partial
$\text{LiOE}_2\text{M/DPMLi}$ (10:1)	$-78$	1	100	15.0	16.1	1.05	yes

<sup>a</sup> taken from Wang et al. (1995 a).

**Table 7-5.** Anionic "random" copolymerization of an MMA-*t*BuA mixture<sup>a</sup> in THF at  $-78^\circ\text{C}$  using (diphenylmethyl)lithium as an initiator and in the presence of various ligands<sup>b</sup>.

Ligand <sup>c</sup>	Time (min)	Yield (wt %)	<i>t</i> BuA in copolymer (mol %)	$M_w/M_n$	Initiator efficiency	Living character
—	60	6.8	87.1	2.5	0.64	no
12CE4	60	25.0	99.0	2.1	0.19	no
$\text{LiCl}$	60	18.2	95.0	2.0	0.33	no
$\text{LiOtBu}$	60	45.0	95.0	2.0	0.41	no
$\text{LiOE}_2\text{M}$	3	100	42	1.15	0.91	yes
DB18CE6 <sup>d</sup>	10	100	42.5	1.1	0.96	yes

<sup>a</sup> Molar ratio in the feed:  $\text{MMA}/t\text{BuA}=58/42$ ; <sup>b</sup> taken from Wang et al. (1995 a); <sup>c</sup> 10 mol. equiv. of ligand relative to initiator; <sup>d</sup> (diphenylmethyl) sodium was used as initiator with 2 mol. equiv. of DB18CE6.



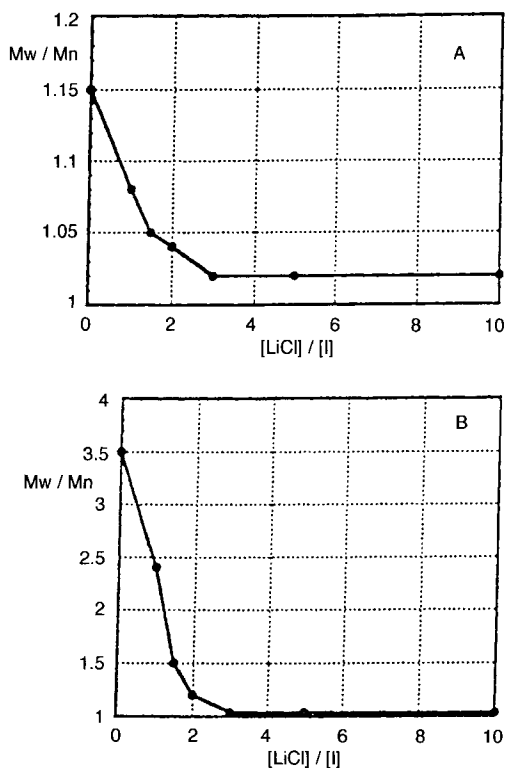
*t*BuA at  $-78^\circ\text{C}$  in THF requires to be living a bulky environment around *t*BuA-based active species in order to avoid their vigorous nucleophilic attack on the very sensitive, small  $\text{OCH}_3$  group. Two sterically more hindered ligated systems, i.e.,  $\text{DB18CE6-Na}^+$  and  $\text{LiOE}_2\text{M-Li}^+$ , efficiently, and for the first time, prevent the aforementioned back-biting attacks [Eq. (7-24)], resulting in well-defined, mono-dispersed, statistical  $\text{P(MMA-co-}t\text{BuA)}$  copolymers (Table 7-5).

### 7.7.3 Effect of Ligands on Kinetics

#### 7.7.3.1 Modification of the Association Equilibria

In contrast to the conventional anionic polymerization of (meth)acrylates, polymerization of MMA and *t*BuA has proven to be free of side termination reactions and quantitative when initiated by diphenylhexyl lithium in THF at  $-78^\circ\text{C}$ . However, the MWD of the resulting poly(meth)acrylate chains usually remains broad and is even multimodal in *t*BuA polymerization (Fayt et al., 1987; Lochmann et al., 1988), as illustrated in Fig. 7-2, the  $M_w/M_n$  of 1.02 and 1.04, respectively.

This evolution reasonably agrees with a significant effect of the ligand on both the initiation and propagation steps, rather than on the termination step. Kinetic (Kunkel et al., 1992) and NMR (Wang et al., 1993 a) investigations support the key effect of asso-



**Figure 7-2.** MWD of (A) PMMA and (B) PrBuA as a function of LiCl-to-initiator molar ratio. Initiator, DPMLi; solvent, THF; temperature,  $-78^\circ\text{C}$ ; yield, 100% [from Wang et al. (1995a)].

ciation-complexation equilibria in the anionic polymerization of MMA and *t*BuA. An equilibrium between dimeric and monomeric living  $\text{PMMA}^-\text{Li}^+$  or  $\text{PrBuA}^-\text{Li}^+$  chains in THF should occur. However, complexation of the active centers by LiCl competes with the association of the living poly(meth)acrylate chains, and shifts the ag-

gregation equilibrium towards the formation of a single mixed species. The formed single active complex can thus give rise to a living polymer of very narrow MWD, i.e.,  $M_w/M_n$  close to 1. Similar observations have recently been achieved for *Pr*BuA initiated with MIBLi in the presence of  $\text{LiOE}_2\text{M}$  (Wang et al., 1994b).

### 7.7.3.2 Modification of the Solvation Equilibria

In pure THF or pure toluene at  $-78^\circ\text{C}$ , the anionic polymerization of *t*BuMA, as initiated by DPMLi, proceeds in a living fashion and yields a narrow MWD (Wang et al., 1995b). However, broad bi- and multimodal MWDs were obtained in THF–toluene mixtures. Moreover, increasing the temperature from  $-78^\circ\text{C}$  to  $0^\circ\text{C}$  promotes a narrower MWD, atypical of termination reactions; indeed at  $0^\circ\text{C}$ , a very narrow unimodal MWD is again obtained. A solvation equilibria mechanism has recently been proposed in order to interpret these observations. There coexist (several) THF-solvated and nonsolvated active species, exchanging slowly compared with the monomer addition rate, but fast at  $0^\circ\text{C}$ , thus resulting in a multimodal MWD in the former case and a narrow one in the latter.

As expected, these slowly exchanging solvation equilibria are affected by the ligation dynamics, so that the MWD of the resulting polymer is also modified. Table 7-6 summarizes the effect of  $\mu$ -,  $\sigma$ -, and  $\mu/\sigma$ -type ligands on *t*BuMA anionic polymerization in a 70:30 toluene–THF mixture at  $-78^\circ\text{C}$ . Again, the much narrower MWD of *Pr*BuMA chains obtained in the presence of LiCl,  $\text{LiOE}_2\text{M}$ , and K211 can be accounted for by their high propensity to coordinate with lithium ester enolates. This results in a fast exchanging ligation equilibrium and the formation of a single type of active complex (Wang et al., 1993a, 1994a, b, 1995a).

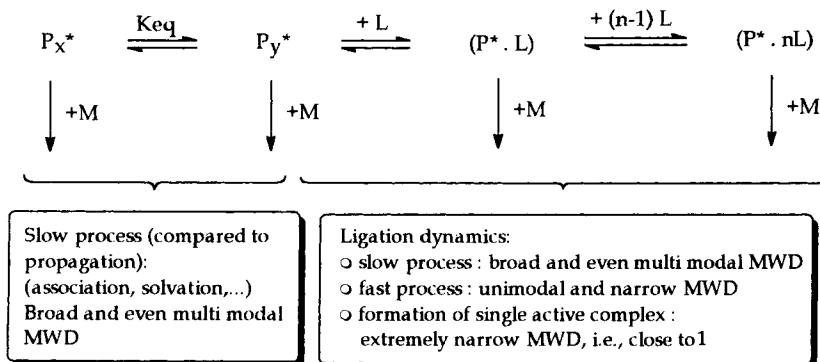
The ligation dynamics therefore control the MWD of the formed poly(meth)acrylate chains by a similar and concomitant effect on the association and solvation equilibria. Scheme 7-4 illustrates how the dynamics of the ligation process may affect the anionic living polymerization (Wang et al., 1995a). It is worthwhile pointing out that such a multi-state dynamic equilibria mechanism also governs the stereochemistry of MMA anionic polymerization (Wang et al., 1993b, 1994c). As far as the MMA polymerization in toluene/THF mixtures is concerned, the following conclusions have been drawn:

- 1) The associated and nonassociated species could selectively produce the meso

**Table 7-6.** Anionic polymerization of *t*BuMA in a 70:30 toluene–THF mixture at  $-78^\circ\text{C}$ , using DPMLi in the presence of various types of ligands (L) ( $[\text{DPMLi}]_0 = 5 \times 10^{-3} \text{ mol l}^{-1}$ )<sup>a</sup>.

Ligand	$[\text{L}]_0/[\text{DPMLi}]_0$	Time <sup>b</sup> (min)	$M_{\text{nsic}}$	$M_w/M_n$	Initiator efficiency
—	—	240	9900	2.00	0.81
12CE4	10/1	150	9500	1.35	0.84
K211	2/1	360	8900	1.05	0.90
LiCl	10/1	60	8200	1.04	0.97
$\text{LiOE}_2\text{M}$	10/1	30	8700	1.03	0.92

<sup>a</sup> Taken from Wang et al. (1995a); <sup>b</sup> 100 wt.% yield.



Scheme 7-4.

and racemic placements, respectively, even though the effect of some intramolecular coordination can not be precluded.

- 2) Complexation of active species by lithium cation-binding ligands, such as 12CE4 and K211, simply shifts the association equilibrium towards the formation of nonassociated species, resulting in syndiotactic placements.
- 3) The effect of a  $\mu$ -type ligand strongly depends on the aggregation degree of the living polymer chains in the formed active complex.
- 4) Since a dual  $\mu/\sigma$  lithium alkoxide,  $\text{LiOE}_2\text{M}$ , promotes the formation of the same type of nonassociated  $\mu/\sigma$  loser complex, whatever the solvent, a highly syndiotactic PMMA results in all cases.

More details, including the PMMA stereoregularity and its likely control by either the E-Z stereoisomerism (Baumgarten et al., 1991) of the living chain end or the "penultimate" mechanism, can be found in a recent review by Teyssié and co-workers (Wang et al., 1995a).

#### 7.7.4 A Golden Tool for Macromolecular Engineering

The efficiency of the "ligated" anionic polymerization (LAP) has been convinc-

ingly established. It allows very fine tuning of the reactivity of the complexed active species, its stability, and to some extent its stereoselectivity, these being the key parameters to be controlled with a view to developing a sufficiently broad and versatile macromolecular engineering.

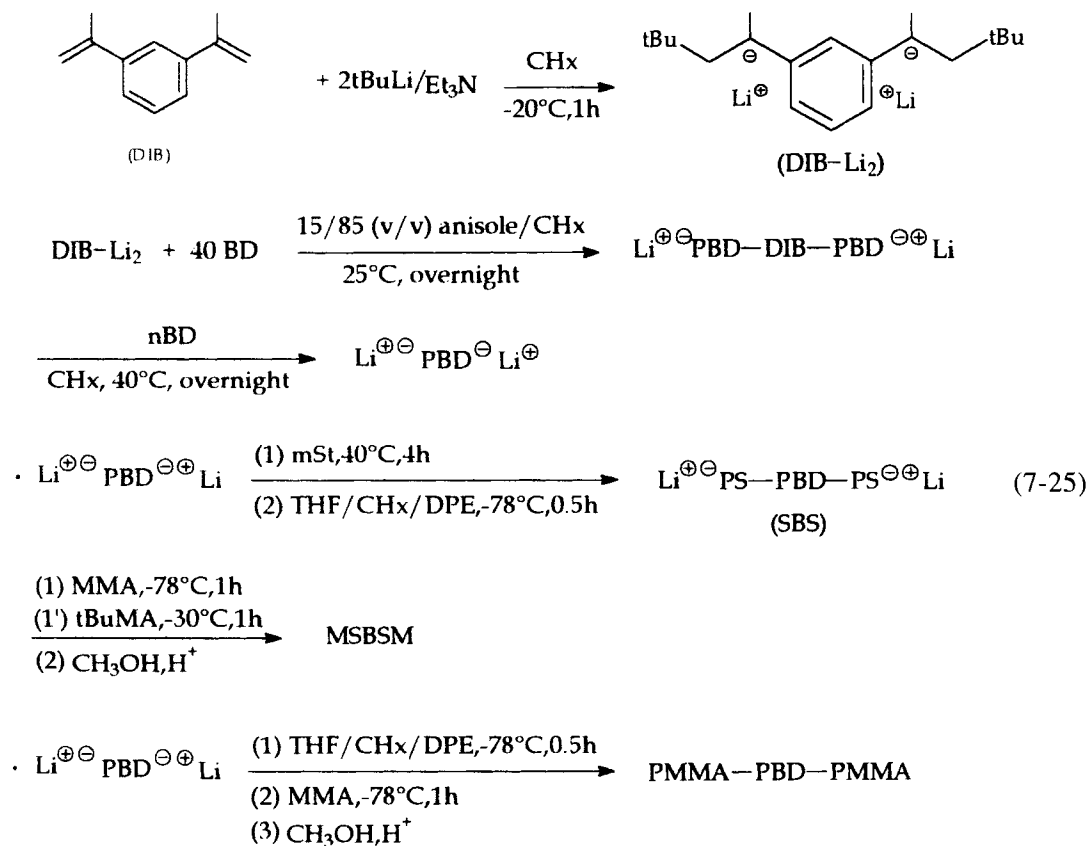
These potentialities have been illustrated by the practical, straightforward synthesis, under convenient solvent and temperature conditions, of the wealth of promising new products:

- monodisperse homo-PMMA ( $M_w/M_n < 1.05$ ) with a high (ca. 80%) syndiotacticity and displaying a  $130^\circ\text{C}$   $T_g$  (Wang et al., 1995a);
- monodisperse polyacrylates and polyacrylic acid, directly obtained from  $\text{PrBuA}$  owing to a easy hydrolysis reaction (Teyssié et al., 1990);
- poly(meth)acrylate macromonomers (Antolin et al., 1990), telechelics (Varshney et al., 1990a), and halatotelechelic with unexpected mesomorphic-type phase organization (Maus, 1994);
- monodisperse random copolymers (Wang et al., 1994d), diblock copolymers with styrenes and dienes useful as emulsifiers and compatibilizers (Hautekeer et al., 1990; Forte et al., 1990);
- triblock (Wang et al., 1994e) and star diblock copolymers (Jérôme et al., 1996).



Undoubtedly, the same approach can also be applied, when necessary, to other monomers susceptible to nucleophilic initiation and attacks, i.e., styrenes, dienes, vinylpyridines, oxiranes, and cyclosiloxanes, in combination or not with (meth)acrylates. A typical example is provided with the well-tailored synthesis of triblock copolymers of styrene and butadiene (SBS), MMA and butadiene (MBM), and even MSBSM five-block copolymers, where B stands for butadiene, S for styrene, and M for either MMA or *t*BuMA (Yu et al., 1996a, b, 1997). These block copolymers have been synthesized by sequential anionic polymerization in apolar and polar solvents using a difunctional anionic initiator derived from 1,3-diisopropylbenzene (DIB) [Eq. (7-25)]. Improved

mechanical properties and an extended service temperature compared to traditional SBS thermoplastic elastomers have been reported for the methacrylate-based copolymers. Upon hydrolysis and further neutralization of the *Pr*BuMA end blocks, the upper glass transition temperature ( $T_g$ ) of the five-block copolymers has been raised up to about 150 °C. A further increase in this service temperature (up to ca. 160 °C) has resulted from the blending of *s*PMMA-SBS-*s*PMMA five-block copolymers with isotactic polymethylmethacrylate (*i*PMMA), due to the formation of a stereocomplex (Yu et al., 1997a). The tensile properties of these modified five-block copolymers have remained essentially unchanged (Yu et al., 1997b).



## 7.8 Conclusions

In the past 10 to 15 years, we have witnessed a spectacular revival of polymer science owing to the huge advances achieved in anionic, or more widely, nucleophilic polymerization. The achievements summarized in this chapter definitively provide confidence in the belief that organic chemistry mechanisms might be applied for the implementation of new polymerization processes. The GTP and aldol-GTP mechanisms represent unique examples of such an application. Similarly, coordination (and organometallic) chemistry principles constitute other golden tools for tailoring active sites in anionic polymerizations and, subsequently, for obtaining the expected macromolecular engineering of the related polymers.

Even though remarkable and substantial progress has been achieved, the field of anionic polymerization still provides the synthetic chemist with fascinating challenges of prime interest. Such challenges could be approached in terms of “molecular engineering of the active anionic sites” by tailoring and tuning their electronic distribution as well as their steric barriers. Targets could be achieved in several directions:

- Controlled polymerization of functional monomers: Key monomers are, among others, acrylonitrile, vinylic, and vinylidene halogenides.
- Control of polymer microstructure and beyond, of their macroscopic properties, such as crystallinity, glass transition temperature, and so forth: A first example of polymer stereochemistry control can already be found in methacrylates polymerization initiated with chiral organolanthanides, as discussed in Sec. 7.6.1. Heaps of possibilities remain, of course, open in this perspective.

- Control of apparent relative reactivities, as typically illustrated by the anionic copolymerization of styrene and butadiene: in a polar medium (THF), a random copolymer is generated as a result of Bernoullian statistics of monomer incorporation whereas, in a hydrocarbon solvent, the polyaddition process yields a tapered copolymer. Surprisingly, this very attractive observation and the concomitant concept have not been explored very much.
- Raising of the relative reactivities: This ambitious challenge is most interesting for the synthesis of triblock copolymers, because this strategy would allow the “malediction” of the decreasing reactivity cascade to be avoided. Indeed, block copolymerizations require the addition of the comonomers in an order rigorously dictated by their relative reactivity toward the active anionic end groups of the polymeric chains previously formed. This reactivity scale usually constitutes a serious limitation in the synthesis of A-B-A, and even A-B-C, triblock copolymers, all the more so since efficient and quantitative coupling methods for living diblock copolymers are hardly available. The main idea should rely upon a tuning up of the active site end-capping of the diblock copolymer, so that it could manage to initiate a more exacting monomer.

The above four examples clearly show that, even though more than 40 years old, the field of anionic polymerization remains rich in unexploited directions and potential technological applications.

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## 8 Cationic Polymerization

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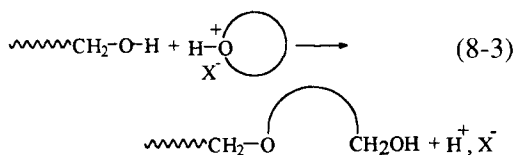
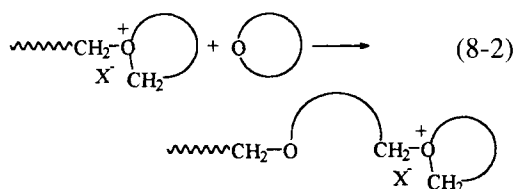
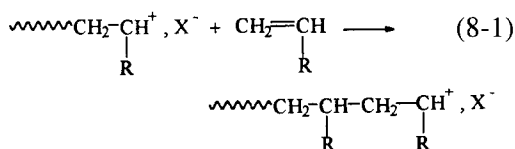
## List of Symbols and Abbreviations

$\overline{DP}_n$	mean degree of polymerization
$G$	free energy
$H$	enthalpy
$K$	equilibrium constant
$K_D$	dissociation constant
$k_i$	initiation rate constant
$K_i$	ionisation constant
$k_p$	propagation rate constant
$k_p^+, k_p^\pm$	propagation rate constant of free cations and of ion pairs
$K_{dp}$	depropagation rate constant
$p\overline{k}_a$	negative logarithm of equilibrium constant for association
$\overline{M}_n$	mean number-average molecular weight
$\overline{M}_w$	mean weight-average molecular weight
$n$	number
$S$	entropy
$T$	temperature
$T_c$	ceiling temperature
Bu	butyl
CEVE	chloroethyl vinyl ether
dp	depropagation
Et	ethyl
EVE	ethyl vinyl ether
IB	isobutene
IBVE	isobutyl vinyl ether
IMA	incremental monomer addition
L. A.	Lewis acid
Me	methyl
MM	molar mass
MMD	molar mass distribution
$M_t$	metal
MVE	methyl vinyl ether
NMR	nuclear magnetic resonance
Nu	nucleophile
NVC	<i>N</i> -vinyl carbazol
p	propagation
Ph	phenyl
PMMA	poly(methylmethacrylate)
Pr	propyl
St	styrene
THF	tetrahydrofuran
TMPCl	2-chloro-2,4,4-trimethylpentane
TMSI	trimethylsilyl iodide
UV	ultraviolet

## 8.1 Introduction

Cationic polymerization can be defined as an addition polymerization reaction involving positively charged active species acting as electrophiles and associated to entities of opposite charge, i.e., the counteranions.

Most of the time, the electrophilic active species is located at the end of the growing chains, while the monomer acts as a nucleophile [Eqs. (8-1) and (8-2)]. However, a reverse situation prevails in some specific cases, typically in the "activated monomer" mechanism [Eq. (8-3)].

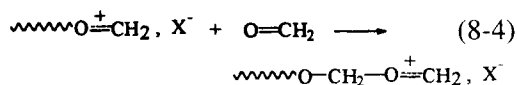


Monomers that polymerize by cationic polymerization may be classified in two main categories:

- 1) ethylenic monomers, for which the reactive entity is assumed to be a carbocationic species [Eq. (8-1)], with the trivalent carbenium ion as the limiting structure, and
- 2) heterocyclic monomers containing one or more heteroatoms within the ring, for which the active species (either the chain end or the activated monomer) is the onium ion (oxonium, sulfonium, phospho-

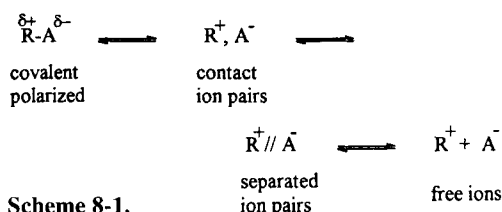
nium, etc., respectively for oxygen, sulfur, phosphorous, etc., as the heteroatom [Eqs. (8-2) and (8-3)]. For onium ions, the central atom has its valence state increased by one unit.

In between these two categories, the polymerization of aldehydes and acetals resembles the carbocationic reaction but involves a strong positive charge delocalization on the neighboring oxygen atom [Eq. (8-4)].



The active species involved in cationic polymerizations can either be clearly identified ions or transient cationic species appearing in the transition state. Covalent species with polarized bonds allowing monomer insertion have also been postulated in the so-called "pseudo-cationic" polymerization. Indeed, a continuous spectrum of ionicities ranging from polarized covalent species to fully dissociated ions (free ions) (Scheme 8-1) has been proposed (Winstein et al., 1956). Obviously, the ionicity of species of a particular system strongly depends on the nature of the two oppositely charged fragments and on the experimental conditions (solvent, temperature etc).

The nature of the interactions between positively charged species and their negative counterparts is very important for the control of cationic polymerizations, since it largely determines the intrinsic reactivity and behavior of the active species. Free carbenium ions, which are often predominant





in traditional carbocationic polymerizations, are highly reactive but unstable and subject to numerous side chain transfer and termination reactions. As a result, it has long been considered almost impossible to synthesize polymers of controlled structure by carbocationic polymerization.

One focal point of “modern” cationic polymerization since the 1980s has been to deal with the ionicity level of active species, with the aim to suppress or at least to considerably limit side reactions and therefore to control the kinetics of the successive elementary events of the chain formation. This approach makes it possible to control the molar mass (MM) (at least over a certain range), the molar mass distribution (MMD), the end-functionality, and the chain architecture, etc, of an increasing number of “cationic-made” polymers.

A series of excellent books for specialists has recently dealt with controlled alkene and heterocyclic cationic polymerization (Kennedy and Maréchal, 1982; Kennedy and Ivan, 1991; Matyjaszewski, 1996). This review is more oriented for advanced students or nonspecialists interested in cationic polymerization. The first section is devoted to carbocationic polymerization, and the new principles developed in the polymerization of ethylenic monomers will be specially examined and illustrated by examples. The basic features of the ring-opening cationic polymerization of heterocyclic monomers, as well as recent developments in this area, will be presented in the last section.

## 8.2 Carbocationic Polymerization of Ethylenic Monomers

### 8.2.1 General Features

Like most chain growth polymerizations, carbocationic polymerization is the com-

bined result of four basic reactions: initiation, propagation, transfer, and termination. The chemistry and kinetic features of these elementary processes will be examined first.

#### 8.2.1.1 Chemistry of Initiation

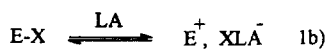
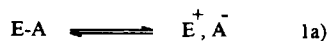
The initiation of carbocationic polymerization generally proceeds in two steps (Scheme 8-2):

- 1) The generation of primary charged species from an initiator, and
- 2) the electrophilic addition of the initiator onto the monomer unsaturation (cationation).

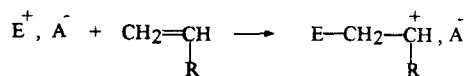
Primary active species are commonly issued from protonic acids, Lewis acids, organic salts, or polarized organic molecules (organic esters or halides). These charged species can form spontaneously by autoionization (Scheme 8-2, reaction 1a) or may require the assistance of a second compound (reaction 1b). Physical methods (ionizing or UV radiation, electric fields, etc.) can also be used to generate primary charged species.

As will be shown in the following sections, the addition rate of the charged initiator fragment ( $E^+$ ) on the alkene (step 2) depends on both the electrophilic character of  $E^+$  and the nucleophilicity (electronic den-

#### 1) primary ion generation



#### 2) cationation



Scheme 8-2.

sity) of the double bond. Stabilization of the resulting carbocationic centers by electro-donating substituents is also crucial to allow ionization and to avoid or limit competitive reactions with other nucleophiles present in the system.

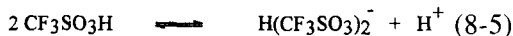
### Initiation by Self-Ionized Species:

#### Protonic Acids:

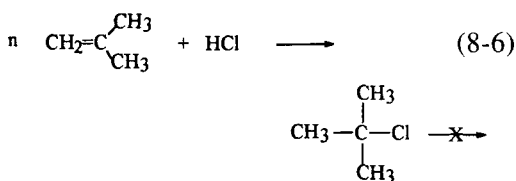
Protonic acids (HX, RCOOH) can initiate the cationic polymerization of ethylenic monomers. Their initiating capacities usually vary with the acid strength (see data in Table 8-1) and depend on the monomer basicity.

The most reactive Brönsted acids are those with the highest acidity (low  $pK_a$ ). This generally corresponds to the lower basicity of their counterions,  $A^-$ . Even for the stronger acids, such as trifluoromethane sulfonic acid (triflic acid), the initiation in chlorinated solvents is a complex process. Polymerization kinetics show high order with respect to the acid (Vairon et al., 1992), indicating that the ionization of one proto-

nic acid molecule involves two or more undissociated acid molecules which aggregate with the anion and the proton [Eq. (8-5)].



Acids with lower acidity (HCl,  $\text{CH}_3\text{COOH}$ ) either do not add onto the monomer double bond or yield covalent inactive monoadducts by rapid recombination of the carbocation with the nucleophilic counterion. The isobutene/HCl system is shown as an example [Eq. (8-6)]. Under similar conditions, initiation of the polymerization of *n*-vinylcarbazole by HCl takes place due to the much lower electrophilic character of the formed species which remains partially ionized (Sawamoto et al., 1987 a).



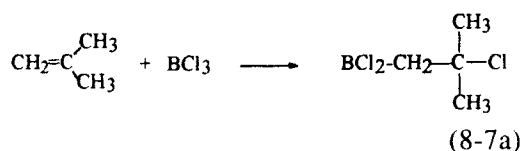
#### Lewis Acids:

Although a more general initiation mechanism will be described later on, in specific cases, metal halides such as  $\text{BCl}_3$ ,  $\text{TiCl}_4$ ,  $\text{AlCl}_3$ ,  $\text{SbCl}_5$ , etc., initiate the polymerization of some ethylenic monomers on their own. The direct addition of  $\text{BCl}_3$  to isobutene was recently demonstrated (Balogh et al., 1994), [Eq. (8-7 a)]. Autoionization of  $\text{AlX}_3$  ( $X = \text{Br}, \text{Cl}$ ) by a 2:2 ionogenic equilibrium [Eq. (8-7 b)], followed by electrophilic addition of the Lewis acid fragment to the monomer has also been proposed (Grattan and Plesch, 1977). However, the initiating efficiency of Lewis acids used alone is extremely low and yields slow and incomplete initiation. The prevailing mode of action is undoubtedly in association with a cationogen (see later).

**Table 8-1.** Estimated  $pK_a$  values of some protonic acids in organic solvents.

Acid	$\text{CH}_3\text{CN}$	$\text{C}_2\text{H}_4\text{Cl}_2$
$\text{ClO}_4\text{H}$	1.6 <sup>a</sup>	3 <sup>d</sup>
$\text{CF}_3\text{SO}_3\text{H}$	2.6 <sup>a</sup>	7.3 <sup>e</sup>
$\text{FSO}_3\text{H}$	3.4 <sup>a</sup>	
IH		7.0 <sup>e</sup>
BrH	5.5 <sup>b</sup>	8.7 <sup>e</sup>
$\text{SO}_4\text{H}_2$	7.3 <sup>b</sup>	
ClH	8.9 <sup>b</sup>	10.8 <sup>e</sup>
$\text{CF}_3\text{COOH}$	10.6 <sup>c</sup>	7 <sup>f</sup>
$\text{CCl}_3\text{COOH}$	12.7 <sup>c</sup>	
$\text{CH}_3\text{COOH}$	22.5 <sup>c</sup>	

<sup>a</sup> Fujinaga and Sakamoto (1977); <sup>b</sup> Kolthoff et al. (1961); <sup>c</sup> Jasinski et al. (1978); <sup>d</sup> Coutagne (1973); <sup>e</sup> Bos and Dahmen (1973); <sup>f</sup> Bolza and Treloar (1972).



### Stable Carbenium Salts:

Direct initiation of carbocationic polymerization by carbenium ions (triphenylmethyl cation, tropylium), stabilized by delocalization and associated to weakly nucleophilic counteranions ( $\text{SbCl}_6^-$ ,  $\text{SbF}_6^-$ ,  $\text{AsF}_6^-$ ), has been extensively investigated. These organic salts, fully ionized in chlorinated solvents, are extremely useful for basic studies. In particular, spectroscopic investigation of the addition kinetics of carbenium ions onto ethylenic monomers permits a comparison of the alkenes' reactivity. Carbenium ions, however, exhibit low reactivities ( $10^{-3}$ – $10^{-6}$  and lower) compared to most of the propagating species, as may be seen in Table 8-2: This irretrievably leads to a slow and incomplete initiation step of the alkene polymerization. Hence stable carbenium ions are not useful for controlled polymerization synthesis.

### Initiation Involving Chemically Assisted Ionization

An important breakthrough in initiation control has been achieved by the use of binary systems formed by the association of a cationogen and a Lewis acid.

### Protonic Acid/Lewis Acid Initiating Systems:

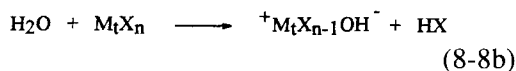
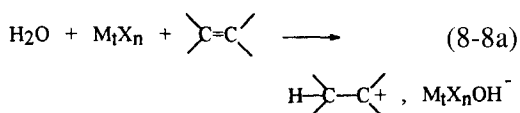
The conjoint participation of a Brønsted and a Lewis acid was first proposed in the so-called "cocatalysis" initiation mechanism as an alternative hypothesis for the initiation by weak Lewis acids of alkene polymerization. The first examples refer to cationic polymerizations in which adventitious water (or an HX impurity) behaves as the protonogen, the Lewis acid playing the role of the activator (or the catalyst) [Eq. (8-8a)]. This scheme, proposed by Plesch et al. (1947), was confirmed in further studies.

The behaviour of  $\text{H}_2\text{O}/\text{M}_1\text{X}_n$  initiating systems is complex, since water can react with both the metal halide, yielding a variety of Lewis acids of decreasing acidity [Eq. (8-8b)], and with the chain end as a terminating agent: The polymerization rate goes through a maximum at a low  $\text{H}_2\text{O}/\text{M}_1\text{X}_n$  ratio and then rapidly decreases for higher proportions of protonogen.

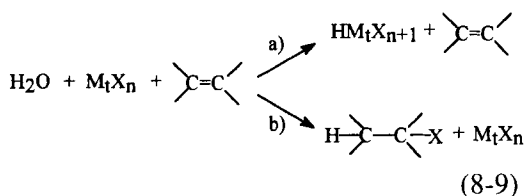
**Table 8-2.** Rate constants of initiation and propagation in the cationic polymerization of some alkene monomers initiated by trityl or tropylium salts.

Monomer <sup>a</sup>	<i>T</i> (°C)	<i>k</i> <sub>i</sub> (mol <sup>-1</sup> L s <sup>-1</sup> )	<i>k</i> <sub>p</sub> (×10 <sup>-4</sup> ) (mol <sup>-1</sup> L s <sup>-1</sup> )	Reference
<i>p</i> -MeOSt	10	0.28	2.8	Cotrel et al. (1976)
α-MeSt	-70	17	2.2	Villesange et al. (1977)
MVE	0	0.6	0.026	Subira et al. (1988)
EVE	0	2.3	0.7	Subira et al. (1988)
IBVE	0	5.4	1.5	Subira et al. (1988)
NVC	20	130	10	Rooney (1976)
St		0.0009 <sup>b</sup>	0.05	Johnson and Pierce (1976)

<sup>a</sup> St: styrene, MVE: methyl vinyl ether, EVE: ethyl vinyl ether, IBVE: isobutyl vinyl ether, NVC: *N*-vinyl carbazole; <sup>b</sup> 30 °C; <sup>c</sup> 0 °C.



Depending on the reaction conditions and on the order of components' addition, different reaction pathways may also take place, leading to different ionic species [Eq. (8-9 a, 8-9 b)]. In controlled cationic polymerization, as detailed in Sec. 8.2.2, path b) is privileged: This is achieved by synthesizing the HX mono-adduct prior to adding the Lewis acid activator. In living vinyl ether polymerization, for example, the protonic acid is reacted first with the monomer to quantitatively give an  $\alpha$ -halogeno ether adduct (Sawamoto and Higashimura, 1986). Initiation of the polymerization is then triggered by ionization of the adduct's carbon-halogen bond by adding a Lewis acid (see Sec. 8.2.2.2).



Indeed, in binary initiating systems the Lewis acid is the catalyst and not (as it is incorrectly called) the cocatalyst, whereas the proton of the Brönsted acid may be considered as the initiator.

#### *RX/Lewis Acid Systems:*

Alkyl halides, arylalkyl halides, or their corresponding organic esters are covalent compounds in commonly used cationic polymerization solvents. However, in the presence of a Lewis acid ( $\text{SnCl}_4$ ,  $\text{AlCl}_3$ , etc.) their cationation may proceed [Eq. (8-10)] and initiate alkene polymerization. When

associated to organic halides or esters, even weak Lewis acids ( $\text{ZnCl}_2$ ,  $\text{BCl}_3$ ) are active initiators.



Indeed, the latter organic compounds may be visualized as adducts of protonic acids (hydrogen halides or carboxylic acids) and alkenes. The RX/Lewis acid initiating systems resemble those involved in the initiation process described in Eq. (8-9 b).

It is worth noting that the relative rates of initiation and propagation will be very close when the RX compounds and the growing ends have almost the same structure. In other cases, i.e., when the initiating fragment has a different structure from the polymer terminal, it is difficult to predict the relative rates of initiation and propagation, since both the ionization ratio and intrinsic reactivity of the species, which vary in opposite directions, contribute to the observed rate.

The efficiency of a series of chloride derivatives (associated with various weak Lewis acids) for the addition of 2-methyl 1-pentene has recently been compared (Mayr, 1989). The best results are observed with chloride derivatives, which lead to both high ionization yields and carbocations of sufficient reactivity. For example, in the series of diarylmethyl chlorides  $(\text{R}_1\text{Ph})(\text{R}_2\text{Ph})\text{CHCl}$ , a gain in electron donation increases the relative reactivity by several orders of magnitude due to a higher degree of ionization. However, the reactivity decreases when carbocations are too stable.

The nature of the associated Lewis acid is also of prime importance. Arylalkyl chloride in conjunction with  $\text{BCl}_3$  leads to polyisobutene with controlled and predicted molar masses, in agreement with the formation of one chain by the chloride derivative, whereas the use of  $\text{BF}_3$  leads to a rapid IB polymerization into polymers with higher

molar masses than predicted, due to incomplete cationation of the precursor.

Cationation of organic esters, ethers, and acyl halides by Lewis acids ( $\text{BCl}_3$ ,  $\text{TiCl}_4$ ) to initiate the polymerization of alkenes (IB) has also been reported. Depending on the structure of the cationogen, initiation can be partial or quantitative (Kennedy and Ivan, 1991).

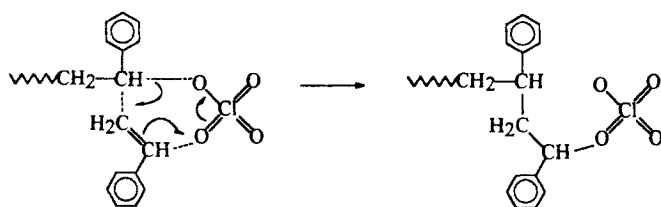
### 8.2.1.2 Propagation

Chain propagation is the repeated reaction between the monomer and the growing polymer with subsequent reformation of the same active species.

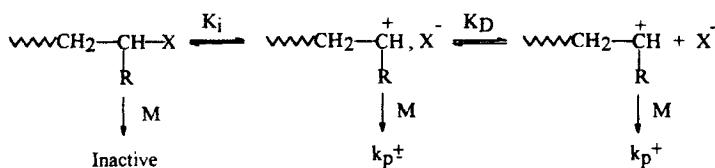
Cationic active centers are identified most of the time as ionic species (contact ion pairs, separated ion pairs, unpaired cations), but polarized covalent species have also been postulated as potential growing species. Polymerizations that proceed via apparently covalent growing ends were postulated in several cases (Gandini and Plesch, 1965; Gandini and Cheradame, 1980). These polymerizations are characterized by a much lower overall reactivity than typical carbocationic systems, as well as by a lesser contribution of side reactions. Whether these covalent species directly react with the monomer via multicenter rearrangement, as

postulated in the pseudocationic polymerization theory (Gandini and Plesch, 1965; Plesch, 1988) (Scheme 8-3), or through intermediate ionic species present in very low concentration (Matyjaszewski, 1987; Williams, 1994) (Scheme 8-4), was the basis of a long controversy. Theoretical considerations and recent experimental results tend to support the second mechanism, which involves the transient and reversible formation of ions as the true active species, whereas covalent species are inactive and serve only as a reservoir.

In systems where covalent ends are in low proportion (conventional carbocationic systems), the cationic propagation rate constants of most alkenyl monomers (at  $0^\circ\text{C}$ ) are in the range of  $10^4$ – $10^6 \text{ mol}^{-1} \text{ L s}^{-1}$  (Matyjaszewski, 1996). In contrast to anionic polymerization of vinyl monomers, where the reactivity between contact and free ions may differ by a factor  $10^5$ , the absolute reactivity of ion pairs and free ions is relatively close (less than a factor of ten). This results from the larger size of the counteranions (low charge density, weak coulombic interaction with the cation) compared to the counteractions ( $\text{Li}^+$ ,  $\text{Na}^+$ ) generally used in anionic polymerizations. The  $k_p$  values of a series of monomers are indicated in Table 8-2. Since, in principle, the



Scheme 8-3.



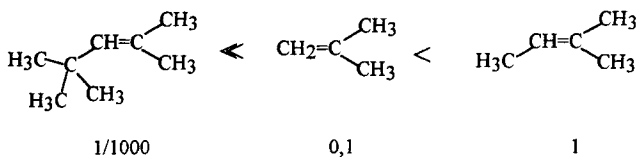
Scheme 8-4.

more stable carbocation corresponds to the more reactive monomer, a leveling off of the reactivity is observed in homopolymerization.

Monomer reactivity orders can be determined either by a study of random copolymerization kinetics or by measuring the addition rate of monomers on a similar nucleophile. Information on reactivities and addition mechanisms obtained by this last approach have recently been reviewed (Mayr, 1996). The general order of reactivity in the alkene monomer series is *n*-vinyl carbazole > vinyl ethers >  $\alpha$ -methyl styrene > styrene > isoprene > butadiene > propylene.

Substituent effects on alkene reactivity are usually discussed in terms of steric and electronic contributions. Important steric effects are mainly found when a bulky substituent is present at the position of electrophilic attack (Mayr et al., 1990), as shown in Scheme 8-5. These effects usually become negligible when the substituents are far from the reaction center. Apart from steric hindrance, electrodonating substituents tend to increase the monomer reactivity. In the styrene series, the reactivity increases with the basicity of the double bond, i.e., *p*-OMe > *p*-Me > *p*-H > *p*-Cl > *m*-Cl  $\gg$  *m*-NO<sub>2</sub>.

In a similar way, the relative reactivity of propagating carbocations was determined by studying their addition rate on a similar  $\pi$ -electrophile. The addition kinetics of cations on a series of alkenes were investigated by Mayr and Striepe (1983).

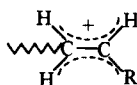


Scheme 8-5.

### 8.2.1.3 Transfer Reactions

Transfer reactions are the most important side reactions in alkene carbocationic polymerization; displacement of the active center from the initial polymer growing end results in the formation of new macromolecules and leads to a decrease of the final polymer molar mass.

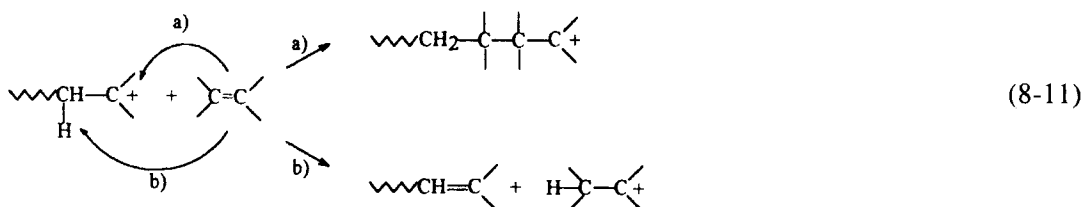
Transfer reactions in cationic polymerizations may be visualized as the competitive reaction between the electropilic polymer ends and the various nucleophiles and bases present in the polymerization system. The former can react either directly through their positively charged carbon or via other neighboring atoms activated by partial displacement of the positive charge (Scheme 8-6).



Scheme 8-6.

#### *$\beta$ -Hydrogen Elimination*

Charge delocalization by hyperconjugation results in an appreciably positive charge on each  $\beta$ -hydrogen atom of the propagating carbenium ions involved in isobutene, vinyl ether, styrene, etc., cationic polymerization. In the case of polystyrene, the charge on the  $\beta$ -hydrogens may reach up to 30% of the total charge (Matyjeszewski, 1996). Indeed, the distribution of the positive charge between  $\beta$ -H atoms and C<sup>+</sup> will determine the relative ability for a terminus to  $\beta$ -transfer or propagate.



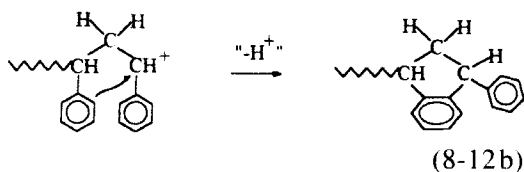
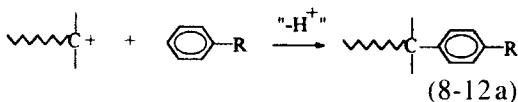
Although spontaneous proton elimination remains unlikely,  $\beta$ -protons are easily abstracted by the monomer and any basic compounds present in the system [Eq. (8-11)].

$\beta$ -H elimination by the solvent or counterion with a basic character may also take place. This is particularly the case for counterions derived from protonic acids. Triflic acid, for example, produces predominantly unsaturated dimers and low molar mass styrene oligomers. Complex metal halides counterions,  $M_nX_{n+1}^+$  should be preferred to limit this type of  $\beta$ -H transfer.

#### Carbocation Reactions

Friedel-Crafts alkylations are another important type of transfer reaction involving the electrophilic alkylation of aromatic rings of the solvent, the monomer, or the polymer with the elimination of a proton. The rate of ring substitution increases with the presence of electrodonating substituents on the aromatic ring and with the charge density of the carbocation.

In the case of aromatic monomers, electrophilic substitution may occur inter- or intramolecularly [Eq. (8-12 a) and (8-12 b)], yielding indanyl end groups in the latter case.



#### Hydride Transfer

The driving force of this reaction is the formation of a more stabilized carbocation [Eq. (8-13)]. Although some of the new carbocations are reactive, in most cases they are too stable and unreactive towards monomers, and therefore hydride abstraction may be seen as a termination reaction.



#### 8.2.1.4 Termination Reactions

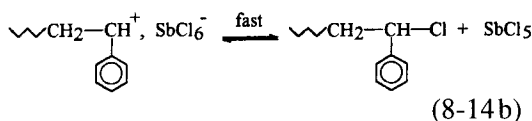
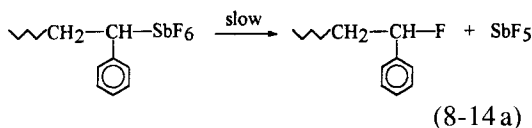
In contrast to transfer reactions for which the charged species expelled from the chain can re-initiate the polymerization, termination reactions are characterized by the disappearance of the positive charge due to recombination with an ion of opposite charge, or by the formation of a stabilized cation which is unreactive towards the monomer. Termination and transfer processes mainly differ by the reactivity of the species formed rather than by the type of mechanism involved.

##### Formation of Stable and Unreactive Carbocationic Species

As already discussed, the possibility for a propagating carbocation to form a more stable cation by abstraction of an ionic fragment ( $\text{H}^-$ ,  $\text{CH}_3^-$ ) is eased by the formation of a more stabilized carbocationic species. Therefore this process tends to preferentially yield unreactive cations.

### *Collapse with the Counterion*

Halides or other ligands of large metal complexes used as counterions can be abstracted by the carbocation, thus forming a covalent species [Eq. (8-14 a, 8-14 b)]. This process is slow in the case of fluoride ligands, but the reaction is irreversible and leads to true termination (Pepper, 1975). On the other hand, in the case of chloride ligands, a fast and reversible abstraction may take place.



### *Reactions with Nucleophilic Impurities and Additives*

Carbenium ions are able to react with nucleophilic compounds. Neutral ones containing heteroatoms generally give unreactive onium ions. However, in the case of weak nucleophiles, this reaction is equilibrated and reversible. Although this equilibrium is shifted to the right, the small fraction of carbenium ions present, constantly renewed, can still propagate. The use of reversible termination to produce well-defined polymers is described in the section devoted to controlled carbocationic polymerization.

Nucleophiles can also react directly with counterions, thus reducing their Lewis acid character [Eq. (8-15)]. In the case of strong nucleophiles, the complexes formed are not

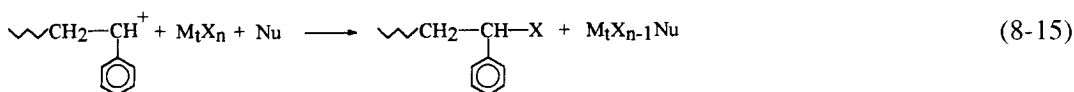
able to ionize the polymer ends and polymerization is stopped. Strong bases may also abstract and trap  $\beta$ -hydrogen atoms, which thus remain inactive towards alkene addition.

Analysis of the chemistry and kinetics of elementary reactions involved in conventional carbocationic polymerization shows that these processes are mainly governed by the interactions between the various nucleophiles and electrophiles present in the system.

Carbenium ions participate in the chemistry of nearly all the elementary reactions. They are very reactive electrophilic species which must be appropriately stabilized by substituents or counterions to allow their formation, prolong their lifetime, and selectively orientate their reaction towards monomer addition. In this respect, strong stabilization by substituents will facilitate their quantitative formation by ionization and will lower the electrophilic character of the carbenium formed, thus limiting side reactions.

The reactivity of carbenium ions towards alkenes approximately follows the variation of charge density on the positively charged carbon atom. Its increase is accompanied by a lower tendency to ionize, whereas hyperconjugation and side reactions are favored.

The aim of "modern cationic polymerization" is to control all the elementary events of the cationic polymerization process by designing systems based on carbenium species of appropriate reactivity in terms of selectivity and kinetics. This means that a procedure developed for a particular system cannot be generalized for another monomer. The general principles of controlled cationic polymerization and their application to





specific polymerization systems will be reviewed in the following section.

## 8.2.2 Principles and Methods of Controlled Cationic Alkene Polymerization

### 8.2.2.1 General Features

A living polymerization is a chain polymerization that proceeds through persistent propagating species without chain-breaking reactions (Szwarc, 1968). Providing that initiation is fast, the molar mass of the polymer is directly related to the molar ratio of monomer consumed to initiator, and the polydispersity of the chains is narrow ( $\bar{M}_w/\bar{M}_n < 1.1$ ). According to this definition, each chain infinitely retains its capacity to add new monomer molecules. After the addition of a new increment of monomer, the polymerization resumes at the same rate and a linear increase of the molar mass is again observed, indicating that the number of active species (no deactivation) and the number of chains (no transfer) are constant during the whole polymerization. Under these conditions, the chemistry of reactive chain ends allowing the preparation of block copolymers, telechelics, and other macromolecular architectures can be developed.

Actually, in real living systems the general characteristics of living polymerization are only fulfilled to a certain extent. In particular, some limited deactivation or transfer reactions may take place (Matyjaszewski, 1993). If they do not affect the final polymer characteristics too much, these polymerizations are often classified as “living”, pseudo living, apparently living, etc. Recently Matyjaszewski proposed the classification of systems allowing the preparation of well-defined polymer structures

under the term of controlled polymerizations.

This chapter aims to discuss the general principles and methods developed in modern carbocationic polymerization to achieve controlled cationic polymerization of alkene monomers.

As discussed in the preceding section, the main side reaction in carbocationic polymerization is chain transfer. This often occurs due to the acidity of the  $\beta$ -H atoms associated to the high delocalization of the carbocationic positive charge. However, another important parameter for the control of carbocationic polymerization involves the kinetics of the initiation and propagation steps (Matyjaszewski and Sigwalt, 1994): Fast and complete initiation should proceed to allow all chains to grow at the same rate.

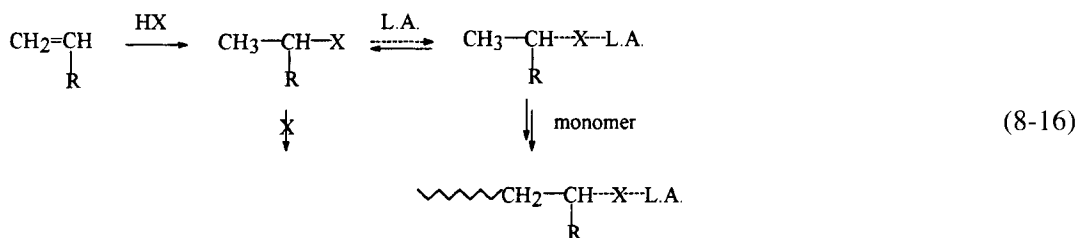
In order to control these parameters in alkene carbocationic polymerization, a series of specific and reversible interactions between the propagating carbocations and various nucleophiles have been used in order to adjust (lower) their reactivity. Three main general approaches have been proposed:

- the use of nucleophilic counteranions,
- the addition of weak nucleophiles,
- the addition of salts.

The different mechanisms involved are described below.

#### *Controlled Polymerization Involving Nucleophilic Counterions*

Polymerizations with  $RX/L.A.$  initiating systems of vinyl ethers (Higashimura and Sawamoto, 1989; Sawamoto, 1991) and isobutene (Kennedy and Ivan, 1991) are typical examples of this type of reaction [see Eq. (8-16)].



RX species are generally obtained by the addition of a protonic acid on the monomer, and therefore possess a structure and reactivity close to those of the polymer chain end. In most cases, these species are covalent and too stable to initiate propagation on their own. However, in the presence of a Lewis acid of appropriate nucleophilicity, which interacts with the terminal halide (or ester), a temporary and reversible ionization of the carbon–X bond occurs, allowing successive monomer insertion. The covalent species are considered as dormant, whereas the active ones are carbocations stabilized via nucleophilic interaction with the counterions (ion pairs). It is important to note that the “appropriate” nucleophilicity of the counterion is strongly related to the nature of the carbocation and monomer. A more detailed presentation of the polymerization pathways involving these systems is given for vinyl ethers and isobutene in Secs. 8.2.2.2 and 8.2.2.4.

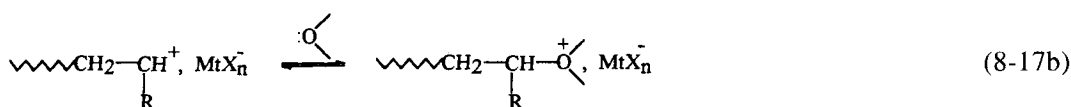
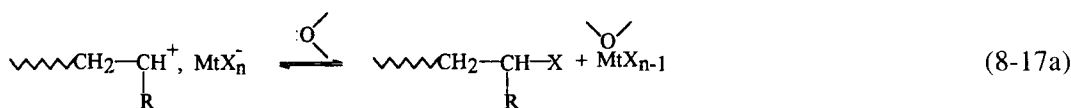
#### Addition of Nucleophiles

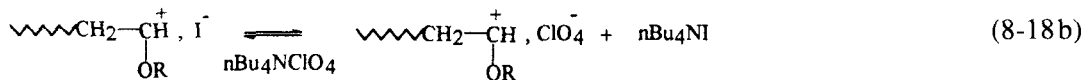
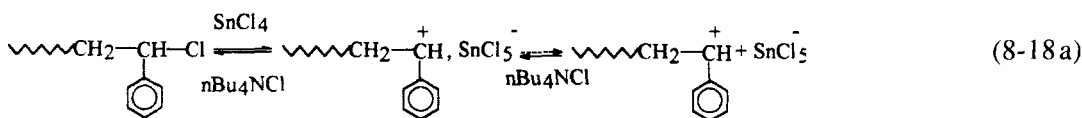
When the counteranion of a polymerization system is too weakly nucleophilic, the equilibrium of the equation is shifted to the

right (active species) and a very fast polymerization takes place. For such systems, it was shown that the addition of an external weak nucleophile (ester, ether, sulfide, etc.) yields better control of isobutene (Kaszas et al., 1988) and vinyl ether (Higashimura et al., 1989a; Higashimura and Sawamoto, 1989) polymerizations. This may be explained by a lowering of the reactivity of the propagating species. This may result from a solvation effect [Eq. (8-17 a)], or more likely from a reduction of the instantaneous concentration of the active species due to the formation of a dormant species [Eq. (8-17 b)]. It has been proposed that the added nucleophiles and the carbocations form onium ions that serve as the dormant species (Matyjaszewski, 1992; Penczek, 1992).

#### Addition of Salts

The use of nonpolar or weakly polar solvents is not sufficient to suppress the contribution of free carbocations to the polymerization. The addition of a common ion salt to reduce the ionic dissociation and allow control of the polymer’s molar mass has been reported for many systems.





Other positive salt effects, operating through different mechanisms and allowing control of the cationic polymerization of vinyl ethers and isobutene, have also been reported. A first series of salts operates by exchanging the counterions for the polymer end groups. The added salt may carry either nucleophilic anions, such as tetrabutyl ammonium halides, which decelerate the polymerization (Higashimura et al., 1993a; Lin et al., 1993) [Eq. (8-18a)] or, on the other hand, less nucleophilic anions, which activate the polymer terminals (Nuyken et al., 1990) [Eq. (8-18b)]. Modification of the nucleophilicity of the counterions by interaction with the anion of the salt has also been proposed in some specific cases.

### 8.2.2.2 Vinyl Ethers

Owing to the presence of an electron-donating alkoxy substituent, vinyl ethers ( $\text{CH}_2=\text{CH}-\text{OR}$ ) are among the most cationically reactive ethylenic monomers. Their polymerization can be initiated by various acidic compounds: protonic acids [ $\text{HX}$  ( $\text{X}=\text{Cl}, \text{Br}, \text{I}$ ),  $\text{CF}_3\text{CO}_2\text{H}$ ,  $\text{CF}_3\text{SO}_3\text{H}$ , etc.), halogens ( $\text{I}_2$ ), metal halides ( $\text{BF}_3$ ,  $\text{BF}_3\text{OEt}_2$ ,  $\text{SnCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{TiCl}_x\text{OR}_{4-x}$ , etc.), halogenated metal alkyls ( $\text{AlCl}_x\text{R}_{3-x}$ ), organic salts [ $\text{Ph}_3\text{C}^+$ ,  $\text{SnCl}_5^-$ ,  $(\text{EtO})_2\text{CH}^+\text{BF}_4^-$ , etc.], etc.

Although the polymerization of vinyl ethers was described a long time ago (Wislicenus, 1878), the preparation of truly “living” poly(vinyl ether)s was first achieved in 1984 (Miyamoto et al., 1984). Isobutyl vinyl ether (IBVE) was polymerized in the

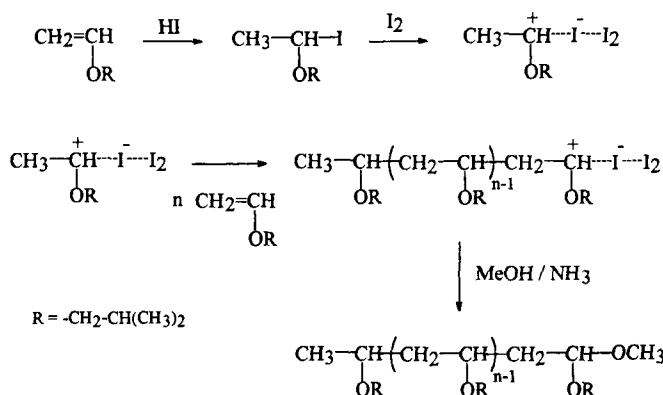
presence of  $\text{HI}/\text{I}_2$  as the initiating system, in a nonpolar solvent and below  $-15^\circ\text{C}$ . The polymerization pathway shown in Scheme 8-7 was finally proposed (Sawamoto and Higashimura, 1986; Higashimura et al., 1988):

- Primary  $\alpha$ -iodo ether compounds are generated by the quantitative addition of hydrogen iodide onto the vinyl ether unsaturation.
- $\alpha$ -iodo ether derivatives are inactive per se and an electrophilic derivative (iodine) should be added to trigger the polymerization.
- The vinyl ether polymerization proceeds by monomer insertion into the “activated” carbon–iodide bonds of  $\alpha$ -iodo ether derivatives.

On these grounds, a series of new initiating systems was thus developed with the aim to prepare well-controlled poly(vinyl ether)s (block copolymers, stars, dendrimers, macrocycles, etc.). Other approaches have also been explored.

#### *Initiating Systems with Nucleophilic Counteranions*

The principle developed in the case of the  $\text{HI}/\text{I}_2$  initiating system has been generalized. It has been shown that combinations of  $\alpha$ -halogeno ethers or  $\alpha$ -carboxy ethers with mild L.A. are also well suited to prepare “living” poly(vinyl ether)s. For example, the polymerization of IBVE initiated by  $\text{HI}/\text{ZnI}_2$  or 2-acetoxyethylvinyl ether/ $\text{ZnI}_2$ , in toluene or  $\text{CH}_2\text{Cl}_2$ , is living in the range



Scheme 8-7.

–40 °C to room temperature (Sawamoto et al., 1987 b). Good agreement between  $\bar{M}_n$  (experimental) and  $\bar{M}_n$  (theoretical, a linear growth of  $\bar{M}_n$  (exp.) with conversion, as well as a narrow MMD are observed. Recently, Kamigaito et al. (1995) showed that isopropoxy-substituted titanium chlorides are also efficient activators for the living polymerization of IBVE initiated by the IBVE–HCl adduct in  $\text{CH}_2\text{Cl}_2$  at –15 °C.

Trimethyl silyl halides associated to carbonyl compounds (Kamigaito et al., 1993 a) or aryl phosphates (Kamigaito et al., 1993 b), and activated by a mild L.A., such as  $\text{ZnX}_2$ , also initiate the living polymerization of vinyl ethers.

#### *Polymerization in the Presence of Added Salts*

The possible effect of common ion salts on the living character of vinyl ether polymerization was well demonstrated in the case of IBVE polymerization initiated by the HCl–IBVE adduct (or  $\text{CF}_3\text{CO}_2\text{H}$ ) and activated by  $\text{SnCl}_4$  in the presence of  $\text{NBu}_4\text{X}$  ( $\text{X}=\text{I}, \text{Cl}, \text{Br}, \text{CH}_3\text{CO}_2$ ) (Kamigaito et al., 1993 c; Katayama et al., 1995 a, b). The authors were able to show the influence of the added salt on the nature of the chain terminals by in situ, direct NMR analysis. They correlated the observed livingness of the

polymerization to the fact that ionic species are not present or detectable in the presence of salts. Cramail and Deffieux (1994, 1995) used the common ion salt effect to induce the living polymerization of very reactive vinyl ethers such as cyclohexyl or isopropyl derivatives. In this case, activation by L.A. is not necessary to start the polymerization, but the addition of tetrabutylammonium iodide in minute amounts ( $[\text{NBu}_4\text{I}]/[\text{HI}]=1/100$ ) is sufficient to shift the equilibrium towards ion pairs and to induce a “living” process. Taking into account the kinetic data, the concentration of active species and  $k_p^+$  and  $k_p^\pm$  values could be estimated.

In addition, it is worth noting that salts may operate according to a different mechanism. The activation of mixed inactive  $\alpha$ -iodo and  $\alpha$ -chloro ether termini by  $\text{NBu}_4\text{ClO}_4$ , involving counteranion exchange, has also been reported (Cramail et al., 1993). It is also worth noting that the combination of triflic acid with tetrabutylammonium iodide was used to generate HI, allowing the controlled polymerization of vinyl ethers (Haucourt et al., 1993). Moreover, poly(IBVE) ( $\bar{M}_n=45\,000$  g/mol,  $\bar{M}_w/\bar{M}_n=1.1$ ), initiated by  $\text{MeCH}(\text{O}i\text{Bu})\text{Cl}/n\text{Bu}_4\text{NTiCl}_5$ , was readily prepared at –20 °C in  $\text{CH}_2\text{Cl}_2$  (Lubnin and Kennedy, 1992).

### *Polymerization in the Presence of Nucleophiles*

In the case of systems for which the counteranions are not nucleophilic enough to stabilize the growing carbocationic species, very fast and uncontrolled polymerization takes place. The addition of an external Lewis base lowers the polymerization rate and may allow control of the reaction. This is the case when a chloro alkyl aluminum is used as the catalyst (typically  $\text{AlEtCl}_2$ ) (Higashimura et al., 1987). The addition of nucleophile (ester, ether, amine, sulfide, etc.) to the system, generally in excess with respect to the initiator, yields a "living" polymerization. Under these conditions, living poly(IBVE)s with high molar mass ( $\bar{M}_n = 10^5$  g/mol) and narrow MMD could be obtained even at a temperature of up to  $70^\circ\text{C}$  (Kishimoto et al., 1989).

In the same way, the first controlled polymerization of *tert*-butylvinylether has recently been achieved using 1-isobutoxyethylacetate/ $\text{Et}_{1.5}\text{AlCl}_{1.5}$ /THF as the initiating system. This method allowed the preparation of polyvinylalcohol with a controlled chain length (Aoshima et al., 1994).

#### 8.2.2.3 Functional Vinyl Ethers

Similar to the alkyl derivatives, a series of side-functional vinyl ethers readily polymerizes in controlled conditions. A detailed list of functional vinyl ether monomers that undergo controlled polymerization is available in several reviews (Sawamoto, 1991; Deffieux, 1996 a). Many studies were per-

formed with 2-chloroethyl vinyl ether, since the chloro function can easily be derivatized into various groups (Higashimura et al., 1984; Nuyken et al., 1995). The synthesis of poly(vinyl ether)s with perfluoroalkyl pendant groups has also been described (Höpken et al., 1992; Vandooren et al., 1994).

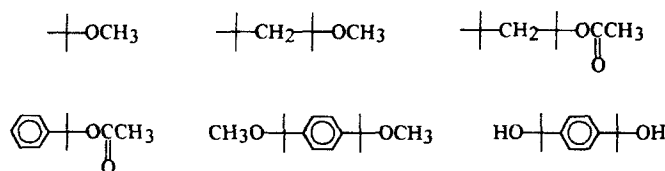
The synthesis of telechelics, block copolymers, and other new architectures based on vinyl ethers is described in the following sections.

#### 8.2.2.4 Isobutene

For many important industrial applications, isobutene (IB) is one of the most attractive hydrocarbon monomers in cationic polymerization. Faust and Kennedy (1986) were the first to report on the "living" polymerization of isobutene. Tertiary acetates (cumyl acetate, 2-acetoxy-2,4,4-trimethylpentane), in conjunction with boron trichloride, were used as the initiating systems (Faust and Kennedy, 1987). As for vinyl ethers, a large number of initiating systems has been described since then.

#### *Systems Involving Nucleophilic Counteranions*

A broad variety of tertiary esters, ethers, and alcohols, activated by  $\text{BCl}_3$ , has been used to initiate the polymerization of IB. Some typical examples are given in Scheme 8-8. Through complexation with the L.A., the carbon–ether or the carbon–ester bond is weakened (ionized), thus allowing monomer incorporation.



Scheme 8-8.

Polymerization is usually performed in mixed solvents ( $\text{CH}_3\text{Cl}/n\text{C}_6\text{H}_{14}$ ; 40/60 vol.) to prevent precipitation of the polymer, and at rather low temperatures ( $-80^\circ\text{C}$  to  $0^\circ\text{C}$ ). Since the overall rates are quite high and transfer to the monomer is important, the incremental monomer addition (IMA technique) has been used. Under these conditions, which avoid or limit chain transfer to the monomer, the polymerization was “quasi-living”.

Nevertheless, even with these systems, the polyisobutene MMDs are generally broader than 1.2 due to some chain transfer and termination reactions. Only recently, it was shown that *tert*-butoxy benzenes (and analogs) activated by  $\text{TiCl}_4$  could initiate the clean polymerization of isobutene. A slight increase of the solvent polarity increases the catalyst efficiency (Flensburg et al., 1995).

#### *Polymerization in the Presence of Added Nucleophiles*

The addition of nucleophiles to initiating systems is frequently employed to avoid side reactions. The combination of tertiary chlorides (cumyl chloride, dicumylchloride),  $\text{BCl}_3$ , and a Lewis base [ $(\text{CH}_3)_2\text{S}=\text{O}$ ,  $(\text{CH}_3)_2\text{NCHO}$ ,  $(\text{CH}_3)_2\text{NCOCH}_3$ ,  $\text{CH}_3\text{COOCH}_2\text{CH}_3$ , etc.] yields truly “living” isobutene polymerization. The nature and concentration of the added base strongly influence the MMD of the polymer (Si and Kennedy, 1994).

Although the presence of a Lewis base is not absolutely required with  $\text{BCl}_3$  as the catalyst, its use is necessary with a stronger L.A. (typically  $\text{TiCl}_4$ ). A proton trap (2,6-di-*tert*-butylpyridine) may also be added to avoid side protic initiation (Gyor et al., 1992).

#### *Initiation in the Presence of Ammonium Salts*

In the case of isobutene polymerization initiated by 2-chloro-2,4,4-trimethylpentane (TMPCl)/ $\text{TiCl}_4$  in a  $\text{CH}_2\text{Cl}_2$ /hexane mixture (60/40), Pernecker et al. (1993) showed that the addition of  $n\text{Bu}_4\text{NCl}$  slows down the apparent propagation rate constants drastically and allows better control of the polymerization.

Macromolecular engineering based on these controlled isobutene polymerizations has been widely investigated and is described in Sec. 8.2.3.

#### 8.2.2.5 Styrene and Derivatives

Although the cationic polymerization of styrene was discovered more than a century ago, the conditions for its “living” polymerization by cationic initiators were only reported in 1988 (Faust and Kennedy, 1988a). Nevertheless, in this first “controlled” system, only polystyrene with a low molar mass was prepared and its MMD was still rather broad.

Since that time, much effort has been devoted to improving the living polymerization of styrene. The rather poorer reactivity of this monomer towards cationic initiators necessitates the use of a strong L.A. to trigger the polymerization. Living conditions were obtained by tuning the interactions between the carbocationic species and added nucleophiles or salts.

Ester compounds activated by  $\text{BCl}_3$  were found to be well suited as initiating systems too (Sigwalt et al., 1988). Ishihama et al. (1990a, b), reported on a polymerization involving 1-phenylethylchloride (or methanesulfonic acid) and  $\text{SnCl}_4$  in the presence of an ammonium salt ( $n\text{Bu}_4\text{NCl}$ ). These systems afford “living” polystyrene with  $\bar{M}_n$  up to  $10^4 \text{ g mol}^{-1}$  and low MMD

$\bar{M}_w/\bar{M}_n = 1.1$ ). The ionic nature of the growing active species, as well as fast exchanges between the halogen termini, were demonstrated by NMR studies (Higashimura et al., 1993a). The effects of ammonium salts on the kinetics and on the MMD of the resulting polystyrene were studied by Lin et al. (1993). Limitations in the living character of these systems, as well as the effect of solvent polarity, were also discussed (Matyjaszewski et al., 1993; Kwon et al., 1993). More recently, Sawamoto and Kamigaito (1995) showed that titanium-based initiators ( $\text{HCl}/\text{TiCl}_3(\text{OiPr})/n\text{Bu}_4\text{NCl}$ ) also allow the preparation of "living" polystyrene in  $\text{CH}_2\text{Cl}_2$  at  $-15^\circ\text{C}$ .

Living poly( $\alpha$ -methylstyrene) could also be prepared using the  $\text{HCl}$  adduct of 2-chloroethyl vinyl ether and  $\text{SnBr}_4$  ( $\text{CH}_2\text{Cl}_2$ ,  $-78^\circ\text{C}$ ) (Higashimura et al., 1993b).

The reactivity of styrene derivatives strongly depends on the nature of the substituent on the aromatic ring; *p*-alkoxystyrenes are the most reactive. Their controlled polymerization can be achieved readily, even at room temperature, in the presence of initiators such as  $\text{HI}/\text{ZnI}_2$  (Kojima et al., 1990a). The living polymerization of *p*-chlorostyrene was first achieved by Kennedy and Kurian (1990). The authors used a combination of 2-chloro-2,4,4-trimethylpentane (TMPCl) and  $\text{TiCl}_4$  as the initiating system in a  $\text{CH}_3\text{Cl}$ /methylcyclohexane mixture (40/60 v/v) at  $-80^\circ\text{C}$ ; the presence of dimethylacetamide as an electron donor and 2,6-di-*t*-butyl pyridine as a proton trap was also required. Recently, Kanaoka et al. (1996) reported that living *p*-chlorostyrene could also be obtained in  $\text{CH}_2\text{Cl}_2$  at room temperature using 1-phenyl ethyl chloride/ $\text{SnCl}_4/n\text{Bu}_4\text{NCl}$  as the initiating system. It is worth noting that in these conditions the polymerization of *p*-chloromethylstyrene and *p*-acetoxymethylstyrene does not exhibit any living character.

The polymerization of alkylstyrenes and related derivatives was achieved using the binary initiating systems  $\text{HI}/\text{ZnCl}_2$  (Kojima et al., 1990b) and  $\text{PhC}(\text{CH}_3)_2\text{OCOCH}_3/\text{BCl}_3$  (Faust and Kennedy, 1988b). Nevertheless, it has to be pointed out that the use of a stronger L.A. is generally required with these monomers than for *p*-alkoxystyrene derivatives.

Finally, it is worth noting that the living polymerization of indene could be obtained using cumyl methyl ether or cumyl chloride in the presence of titanium derivatives (Thomas et al., 1995).

### 8.2.3 Macromolecular Engineering by Carbocationic Polymerization

The discovery that alkenyl monomers can be polymerized in controlled conditions rapidly led to the development of new, tailor-made polymers. The synthesis by cationic techniques of functional polymers, telechelics, block and graft copolymers, star-shaped polymers, and macrocycles is examined below.

#### 8.2.3.1 Synthesis of End-Functionalized Polymers

##### *Functional Initiation*

The anchorage of a functional group at the chain head can be achieved using functional initiators, provided the function is inert or protected.

##### *Vinyl Ethers:*

Typically, this method consists of adding a stoichiometric amount of protonic acid onto a functional vinyl ether (initiating step).

The propagation step is then performed with the desired vinyl ether monomer. A very large series of poly(vinyl ether)s bearing an organic function or a polymerizable group at the chain head (macromonomer) has been prepared accordingly (Sawamoto, 1991; Deffieux, 1996 a).

In the same way, the use of trimethylsilyl iodide (TMSI) in conjunction with a carbonyl or an acetal compound as the initiating system enables the preparation of  $\alpha$ -hydroxy poly(vinyl ether)s (Kamigaito et al., 1990; Meirvenne et al., 1990; Cramail et al., 1994).

#### *Styrene and Derivatives:*

The synthesis of  $\alpha$ -chloro polystyrene starting from  $\text{Cl}_2/\text{AlMe}_3$  or  $\text{BrC}(\text{CH}_3)_2$  as the initiating system was first described by Kennedy and co-workers (Kennedy and Sivaram, 1973; Kennedy and Melby, 1975). More recently,  $\alpha$ -functional poly(styrene)s, poly(*p*-methylstyrene)s (Miyashita et al., 1994 a), poly(*p*-chlorostyrene)s (Kanaoka et al., 1996), and poly( $\alpha$ -methylstyrene)s (Higashimura et al., 1993 b) were synthesized by initiation of the polymerization by a functional vinyl ether–hydrogen halide adduct in the presence of  $\text{SnCl}_4$  and an ammonium salt. Through this procedure, benzoate, acetate, phthalimide, and methacrylate groups could be anchored at the chain head. Following the same principle,  $\alpha$ -hydroxy,  $\alpha$ -carboxy,  $\alpha$ -amino, and poly(*p*-methoxy- and *p*-tert-butoxystyrene)s can be readily prepared (Shohi et al., 1992 a).

#### *Isobutene:*

The head-functionalization of polyisobutene chains has been widely investigated by Kennedy and his group (Kennedy and Ivan, 1991). Various routes yielding  $\alpha$ -hydroxy polyisobutenes have been reported; one recent example deals with the direct addition of  $\text{BCl}_3$  onto the monomer. Derivatization of the  $\text{BCl}_2$  head group into hydroxyl is then achieved by treatment with  $\text{H}_2\text{O}_2$  (Balogh et al., 1994).

Unsaturated or chloride head groups were easily anchored in the presence of a functional cationogen used in conjunction with an L.A. A phenol group was selectively anchored using *p*-hydroxycumylchloride as the initiator in association with  $\text{HCl}/\text{BCl}_3$  (Balogh et al., 1994). The preparation of polyisobutene macromonomers with a styrenyl or a dicyclopentadienyl head group has also been described (Kennedy and Ivan, 1991).

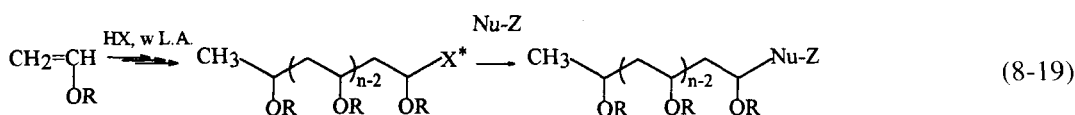
#### *Functional Termination*

This technique is particularly useful provided the polymerization exhibits a “living” character (absence of transfer and termination reactions) and the propagating ends are reactive enough.

#### *Vinyl Ethers:*

The preparation of  $\omega$ -telechelic poly(vinyl ether)s can be readily achieved by quenching the growing chains with a nucleophile bearing a functional group [Eq. (8-19)].

The addition of alcohols onto  $\alpha$ -halogeno ether polymer ends yields acetal terminals which may be further quantitatively de-





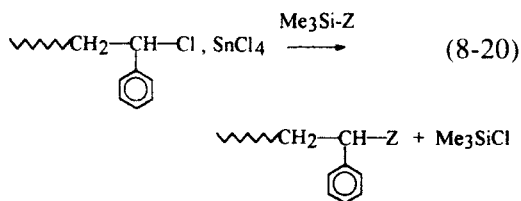
rivatized into aldehyde functions (Bennevault et al., 1995). The latter may also be transformed into alcohol groups after reduction with a metal hydride.

Poly(vinyl ether)s were successfully end-capped by amino groups using various amines in large excess. The use of substituted anilines allowed the preparation of  $\omega$ -hydroxyl- and  $\omega$ -carboxyl-poly(alkyl vinyl ether)s (Sawamoto et al., 1987c). The preparation of stable carboxylic acid end groups by deactivation of the polymer chain with a sodiomalonic ester  $[\text{NaCH}(\text{CO}_2\text{Et})_2]$  was also described (Sawamoto et al., 1987d). Following the same technique, vinyl ether macromonomers of isobutyl and 2-benzoyloxyethyl vinyl ethers were prepared (Sawamoto et al., 1986).

#### Styrene and Derivatives:

*p*-Alkoxystyrenes exhibit a reactivity close to those of vinyl ethers. Therefore,  $\omega$ -telechelic poly(*p*-alkoxystyrene)s are easily prepared (Higashimura et al., 1989b).

$\omega$ -Functionalization of cationic polystyrene is much more difficult due to the higher nucleophilic character of the halide terminal, which stays attached to the chain end, thus forming a *sec*-benzylic halide terminus. Typically, conventional nucleophiles (methanol, amines, sodiomalonnate, etc.) failed to react with the growing polystyrene chain. To overcome this drawback, Miyashita et al. (1994b) recently reported the use of various end-capping agents based on organosilicon compounds ( $\text{Me}_3\text{Si-Z}$ ,  $\text{Z} = \text{acetoxyl, allyl, methacryloxy}$ ) [Eq. (8-20)].



#### Isobutene:

$\omega$ -Functionalization of polyisobutene has been widely studied by Kennedy's group (Kennedy and Ivan, 1991). As mentioned earlier for styrene, the presence of chlorine in the initiator or in the catalyst yields poly(isobutene)s with *tert*-butyl chloride termini. Nevertheless, the synthesis of allyl-capped poly(isobutene) was achieved by quenching the chain termini with allyltrimethylsilane and allyltrimethylstannate (Ivan and Kennedy, 1990).

Other types of  $\omega$ -functionalized poly(isobutene)s were prepared by post-polymerization reactions through derivatization of the tertiary chlorine termini.  $\omega$ -Hydroxyl,  $\omega$ -carboxyl,  $\omega$ -phenyl (phenol, tolyl), or  $\omega$ -epoxy polyisobutene was obtained. From these derivatives, a very large series of new polymeric materials can be prepared (Kennedy and Ivan, 1991).

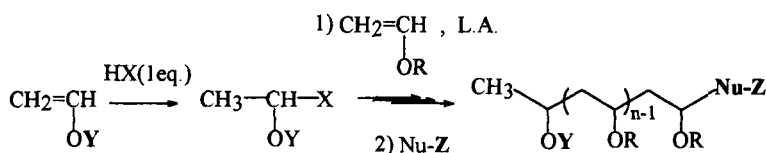
#### Synthesis of Telechelics

Telechelics and more generally pluri end-functional macromolecules are interesting precursors of multiblock structures and networks. Two main approaches have been developed to prepare telechelics:

- multifunctional growth followed by functional termination, and
- functional initiation of the polymerization and termination by the addition of functional molecules.

#### Vinyl Ethers:

$\alpha, \omega$ -Difunctional poly(vinyl ether)s were readily obtained by bifunctional initiation using divinyl ethers/HX or diacetal compound/TMSI systems (Bennevault et al., 1995). Dicumylhalides have also been described as difunctional precursors (Schapacher and Deffieux, 1991).



Scheme 8-9.

The preparation of hetero telechelics bearing distinct  $\alpha$ -Y or  $\omega$ -Z end groups was also reported (Shohi et al., 1990). Their synthesis is depicted in Scheme 8-9. The preparation of telechelic three branch star poly(vinyl ether)s starting from a trivinyl ether precursor, activated by  $\text{AlEtCl}_2$ , has also been described (Shohi et al., 1991).

#### Styrene and Derivatives:

Access to telechelic polystyrenes (with functional groups different from the chloride termini) is more limited by the cationic technique for the reasons previously discussed. Chloro-telechelic poly(*p*-chlorostyrene) prepared from dicumylchloride/ $\text{BCl}_3$  has been described by Zsuka and Kennedy (1991).

In the series of poly(*p*-alkoxy styrene)s, for which the end group is more labile,  $\alpha$ , $\omega$ -homo and hetero-telechelics were prepared using the association of both the functional initiation and termination steps (Shohi et al., 1992b): Functional initiation involved  $\alpha$ -functional halogeno ether adducts activated by  $\text{ZnCl}_2$ , whereas end-capping of the polymer was performed with various functional nucleophiles.

Following the same procedure,  $\alpha$ -functional,  $\omega$ -chloro telechelic poly(styrene) and poly( $\alpha$ -methylstyrene) were obtained (Miyashita et al., 1994a). Recently, Cloutet et al. (1994) synthesized a hexa-armed polystyrene with chloride termini from a precursor composed of six 1-phenylethyl chloride groups.

#### Isobutene:

The preparation of multitelechelic poly(isobutene) has been extensively studied. A series of chain initiators bearing different functions ( $\text{X} = \text{Cl}, \text{Br}, \text{OCH}_3, \text{OAc}, \text{or OH}$ ) is reported in recent reviews (Kennedy and Ivan, 1991; Deffieux, 1996a).

#### 8.2.3.2 Synthesis of Block Copolymers

The synthesis of block copolymers is of great interest, since it allows the preparation of amphiphilic or novel thermoplastic elastomeric materials.

##### Sequential Living Polymerization

A monomer, A, is first polymerized to give a living polymer from which the polymerization of a second monomer, B, is initiated. The use of difunctional initiators gives B-A-B triblock copolymers. The sequential living polymerization of a series of vinyl ethers (typically an alkyl vinyl ether for block A and a pendant functionalized vinyl ether for block B) has been described with  $\text{HI}/\text{I}_2$  or  $\text{HI}/\text{ZnX}_2$  as the initiating system (Miyamoto et al., 1985). Derivatization of the protective side functional groups (block B) into a polar function yields new amphiphilic diblock copolymers (Sawamoto, 1991).

The same type of initiating system was used to induce the sequential polymerization of a vinyl ether (block A) and an alkoxy styrene (block B) (Sawamoto, 1991). Since then, many other block copolymers have been obtained: poly(*N*-vinylcarbazole-*b*-

IBVE) (Nuyken et al., 1995), poly(CEVE-*b*- $\alpha$ -methylstyrene) (Sawamoto et al., 1994), poly(styrene-*b*-methyl vinyl ether) (Ohmura et al., 1994). The preparation of amphiphilic star-shaped block copolymers based on two distinct vinyl ethers was described by Kanaoka et al. (1993).

The literature is particularly abundant in the case of copolymers possessing one poly(isobutene) block: poly(isobutene-*b*-methyl vinyl ether) (Pernecker et al., 1992), poly(isobutene-*b*-isobutyl vinyl ether) (Hadjikyriacou and Faust, 1995), poly(isobutene-*b*-isoprene) (Kaszas et al., 1992), poly(isobutene-*b*-styrene) (Faust, 1994), poly(isobutene-*b*-*p*-methyl styrene) (Nagy et al., 1995), etc.

The preparation of thermoplastic elastomers such as poly(indene-*b*-isobutene-*b*-indene) (Kennedy et al., 1993), or poly( $\alpha$ -methylstyrene-*b*-isobutene-*b*- $\alpha$ -methylstyrene) (Tsunogae and Kennedy, 1994) is also described.

In addition, Verma et al. (1991) reported the preparation of the PVE-*b*-PMMA block copolymer using a combination of living cationic and group transfer polymerizations.

#### *Reaction of End-Functionalized Polymers*

A very large number of block copolymers was prepared from end-functionalized chains. Depending on the functionality of the starting polymers, three approaches were developed to obtain block copolymers: polymerization from a macro-initiator, polymer coupling, and chain extension. An exhaustive list of copolymers obtained from these different routes was recently published (Matyjaszewski, 1996).

Copolymerization of monomer B from a macro-initiator is illustrated by the following examples: cationic ring-opening polymerization of 2-ethyloxazoline from

an  $\omega$ -2-chloroethyl ether poly(IBVE) (Liu et al., 1993), cationic polymerization of vinyl ethers from  $\alpha$ -acetal polystyrene (Cramail et al., 1994), and radical polymerization of methacrylonitrile from an  $\alpha$ -azo poly(IBVE) (Nuyken et al., 1988).

Polymer coupling was used to prepare poly(isobutene-*b*-methylmethacrylate) copolymers through the termination of living carbocationic polyisobutene by living PMMA obtained by group transfer polymerization (Takacs and Faust, 1995).

Finally, novel thermoplastic elastomeric polyisobutene-*b*-polyamide multiblocks were obtained by the chain extension technique (Zaschke and Kennedy, 1995).

#### **8.2.3.3 Star-Shaped and Macrocyclic Polymers**













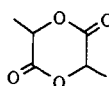


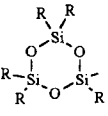
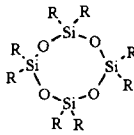
A broad series of star-shaped poly(vinyl ether)s and polystyrene have been prepared using cationic techniques. In addition, the synthesis of macrocyclic polymers of controlled ring dimension based on the cationic reaction has also been reported recently (Deffieux, 1996b).

### **8.3 Cationic Polymerization of Heterocyclic Monomers**

Owing to the nature of the heteroatoms and of the ring strain, heterocyclic compounds containing one or several heteroatom(s) in their structure may polymerize the ionic ring-opening reactions. The main heterocyclic monomers that polymerize by cationic mechanisms are listed in Table 8-3.

Cationic heterocyclic polymerizations usually involve nucleophilic attack of the monomer on a tertiary onium ion located at the chain end [Eq. (8-2), Sec. 8.1]. However, a reverse situation involving the nu-

**Table 8-3.** Some of the main heterocyclic monomers that can polymerize by a cationic mechanism.

Main families	Number of atoms in the ring <sup>a</sup>				
	3	4	5	6	8
Cyclic ethers	 oxirane (117)	 oxetane	 oxolane (28,0)		
Cyclic sulfides	 thiirane (77,8)	 thietane (79)	 tiolane (4,1)		
Cyclic amines	 aziridine (99,1)	 azetidine			
Cyclic acetals			 1,3-dioxane	 1,3,5-trioxane	
Cyclic esters		 β-propio- lactone	 ethylene carbonate	 lactide	
Cyclic iminoesters			 1,3-oxazoline		
Cyclosiloxanes				 D3 <sup>b</sup>	 D4 <sup>c</sup>

<sup>a</sup> The numbers in parentheses correspond to ring strain energies (kJ/mol) (Cox, 1963); <sup>b</sup> D3: hexamethyltrisiloxane; <sup>c</sup> D4: octamethyltetrasiloxane.

cleophilic attack of a heteroatom of the chain end on the protonated monomer (secondary onium ion) may also take place in some cases [Eq. (8-3), Sec. 8.1].

The first major difference between heterocyclic ring-opening and alkene polymer-

ization is the conservation of nucleophilic sites in the polymer chain after the polymerization of heterocyclic monomers, whereas the alkene double bond is consumed during the reaction in alkene polymerization. The presence of nucleophilic heteroatoms en-

ables the polymer backbone to react with electrophilic entities including propagating species through a series of reactions, intrinsic of heterocyclic ring-opening polymerization systems. The relief of monomer ring strain during insertion is the main driving force for ring-opening polymerizations. For example, in the ether, sulfide, and amine series, three- and four-membered rings readily polymerize, whereas the corresponding heterocycles with five, six, or seven atoms of lower ring strain are not polymerizable in normal conditions.

Several books and reviews dealing with the cationic polymerization of heterocycles may be found in recent literature (Allen and Bevington, 1989; Matyjaszewski, 1996).

### 8.3.1 General Features of Cationic Ring-Opening Polymerization

#### 8.3.1.1. Chemistry of Initiation

As indicated for alkenes, initiation of the polymerization may involve several elementary reactions to generate from a primary species an active center with a structure identical to the propagating one. The main families of compounds that are able to generate primary species are presented below.

##### *Protonic Acids*

Stronger acids with weakly basic counterions, triflic acid, fluorosulfonic acid, perchloric acid (see  $pK_a$  values in Table 8-1, Sec. 8.2), are generally the best initiators. This may be explained by the rapid addition of the acidic proton on the nucleophilic heteroatom of the monomer and the formation of stable onium ions. Although weaker acids ( $HX$ ,  $X=Cl, Br, I$ ) may also rapidly and quantitatively add onto heterocyclic

monomers, their nucleophilic anions rapidly recombine with the onium ions to form covalent species, which are usually inactive towards the ring-opening of heterocycles. Only the more nucleophilic monomers, such as oxazolines, are polymerized in the presence of  $Br^-$  or  $I^-$  counteranions (Saegusa et al., 1976).

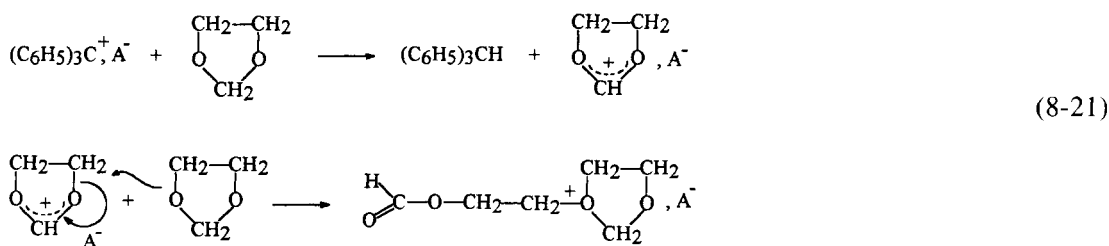
##### *Lewis Acids*

A large number of Lewis acids, used as such or in the form of stable ether complexes, have been reported to initiate the cationic polymerization of heterocyclic monomers.  $BF_3$ , for example, is commercially available in the form of its ether complex ( $BF_3 \cdot OR_2$ ).

In fact, the initiating efficiency of Lewis acids is low and their reaction mechanism with heterocyclics often remains unclear. Direct initiation, though claimed, is not supported by experimental evidence. In most cases, it is believed that the protonogen present, i.e.,  $H_2O$ , plays the role of initiator, the Lewis acid acting as the catalyst (Collins et al., 1979; Stasinski and Dmowska, 1987).

##### *Stable Organic Salts*

A series of stable carbenium, oxocarbenium, and carboxonium ions, stabilized by charge delocalization, have been used to initiate the polymerization of heterocyclic monomers. Most of them directly react with heterocycles to form an oxonium ion. However, some initiation reactions are more complex and involve hydride or proton abstraction, as shown below for the polymerization of 1,3-dioxolane by a trityl salt [Eq. (8-21)] (Penczek and Kubisa, 1973).



### Alkylating or Acylating Agents

Covalent esters of strong protonic acids (triflic, fluorosulfonic, etc.) or their anhydride are able to directly initiate the polymerization of weakly nucleophilic monomers (ethers, siloxanes, acetals). In the same way, trimethylsilyliodide and trimethylsilyltriflate initiate the polymerization of oxazoline.

### Compounds Activated by Anion Exchange or Lewis Acids

Brönsted acids, covalent organic halides, or esters, which are inactive or too weakly reactive to give efficient initiating systems, can be activated in situ by anion exchange (Olah and Von R. Schleyer, 1973) or by the addition of a Lewis acid (Olah, 1965). For example, a series of reactive oxocarbenium and carboxonium can be prepared in situ by the silver salt method [Eq. (8-22)].



Alkyl halides or acyl halides may also be readily ionized by fluorine-containing Lewis acids through the formation of stable and weakly nucleophilic counteranions of the type  $\text{MtF}_n\text{X}^-$ .

As previously mentioned for alkenes, the use of binary initiating systems allows the formation of reactive ionic species yielding fast and efficient initiation of the heterocyclic polymerization.

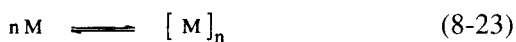
### 8.3.1.2 Propagation Reaction

A distinction should first be made between the reactivity of a monomer and its polymerizability. The latter is related to the thermodynamics of the system and should be distinguished from the kinetics of polymerization. For example, a highly reactive monomer may exhibit a low polymerizability; in which case, a small fraction of polymer rapidly forms and stays in equilibrium with a large fraction of the unreacted monomer.

Let us first examine the parameters governing the thermodynamic behavior in heterocyclic ring-opening polymerization systems.

#### Thermodynamics of the Propagation Reaction

The thermodynamics of heterocyclic ring-opening polymerization have been examined in several recent reviews (Penczek, 1989; Kubisa, 1996). Conversion of a monomer into polymer [Eq. (8-23)] is only possible when the change of free energy accompanying the propagation,  $\Delta G = \Delta H - T\Delta S$ , is negative.

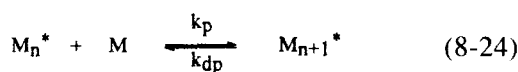


In heterocyclic ring-opening polymerization, the propagation driving force (p) is the negative enthalpy variation corresponding to ring strain release of cyclic monomers, whereas the entropy term ( $-T\Delta S$ ) generally favors the reaction in the opposite way (dp).

The entropy variation accompanying heterocyclic polymerization is mainly due to the loss of translational entropy of the monomer, and only weakly depends on the heterocyclic monomer structure. On the other hand, the enthalpy of polymerization is strongly related to the monomer ring strain. The latter results from several structural parameters, i.e., nonbonded repulsions between atoms, bond angle distortions, and bond length deformations. As may be seen in Table 8-3, the nature and the number of heteroatoms in the ring strongly affect the strain energy. For monomers constituted of carbons and one heteroatom, the strain is usually maximal for three- to four-membered rings and becomes minimal for five- to seven-membered rings. It then increases again for larger rings (8–12) due to transannular interactions.

The enthalpy ( $\Delta H$ ) of polymerization of a system, is practically independent of the temperature, whereas the term  $-T\Delta S$  obviously increases with temperature. Therefore, at a certain "ceiling" ( $T_c$ ),  $-T\Delta S$  will finally equal  $\Delta H$ , thus yielding  $\Delta G=0$ .

At  $T_c$  ( $T_c = \Delta H/\Delta S$ ) and above, the polymerization is prohibited. Considering that the propagation is a reversible process [Eq. (8-24)], this may be visualized by the predominance of the depolymerization reaction, where



$k_p$  and  $k_{dp}$  are respectively propagation and depolymerization rate constants, and  $K$ , the equilibrium constant, is equal to  $k_p/k_{dp}$ .

At equilibrium, we can write

$$k_p [M_n^*][M_e] = k_{dp} [M_{n+1}^*]$$

where  $[M_e]$  is the equilibrium monomer concentration, and since for polymers  $[M_n^*]$  may be assumed identical to  $[M_{n+1}^*]$

$$k_p/k_{dp} = K = 1/[M_e]$$

On increasing the reaction temperature,  $[M_e]$  increases and finally equals the monomer concentration in the bulk. This temperature corresponds to the ceiling temperature at which the polymerization cannot proceed anymore. Note that another definition of the ceiling temperature corresponding to standard conditions is also used. In this case,  $T_c$  is equal to  $\Delta H^\circ/\Delta S^\circ$ , which refers to solution polymerizations with  $[M]_0 = 1 \text{ M}$ .

The second equation shows that at any temperature there is a limit to the monomer concentration corresponding to  $[M_e]$ , under which the polymerization does not occur ( $k_p[M_e] < k_{dp}$ ). If the initial monomer concentration is higher than  $[M_e]$ , the polymerization takes place but then stops (equilibrates) at a partial monomer conversion corresponding to  $[M_0] - [M_e]/[M_0]$ , for which  $k_{dp}$  equals  $k_p[M_e]$ .

### Nature and Reactivities of Active Species

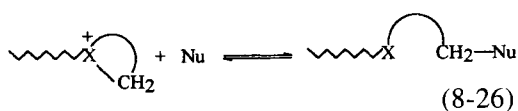
Active species involved in the ring-opening polymerization of heterocycles are mainly onium ions. However, polymer chains with carbenium ions or covalent ester terminals, resulting from the transformation of onium ions, may also be present. The relative contributions of these different polymer end groups to the ring-opening polymerization reaction have been investigated by several research groups.

The first equilibrium exists between cyclic onium ions and their opened form corresponding to carbenium ions (Penczek, 1989) [Eq. (8-25)]. The equilibrium is determined by the balance of energies corresponding both to the release of ring strain, which favors the carbenium ion form, and to the strong stabilization gain when going from high energy carbenium ions to much more stable onium ions. Generally, this second effect exceeds by far the strain release

of the usual heterocycles, and the proportion of carbenium ions is extremely small. Despite the much higher reactivity of carbenium ions, their contribution to the polymerization is usually negligible (Penczek and Szymanski, 1980). In the most favorable situations, such as in the polymerization of cyclic acetals, the contribution of carbenium ions to the propagation reaction was evaluated as a few percent.



Located on the other side of the Winstein equilibrium, chains with a covalent end group have also been identified in ring-opening polymerization systems. These terminals are formed by the recombination of ionic ends (onium or carbenium ions) with their counterion [Eq. (8-26)]. When the latter is a strong nucleophile, the reaction may be irreversible and terminate the polymerization. However, since heterocycles are highly nucleophilic monomers, they may compete with the collapsed counterions and insert in the covalent bond. It was proposed that an ionic chain end is then reformed after the monomer insertion (Penczek and Kubisa, 1993). In this case, covalent polymer ends may still be considered as active species. Their reactivity is, however, much lower than that of onium (and carbenium) ions (Penczek and Matyjaszewski 1976; Saegusa et al., 1976) except in some very particular cases (Baran et al., 1983).



Hence onium ions are the predominant active species in most cationic ring-opening heterocyclic polymerizations. They can exist in the form of ion pairs and free ions; their

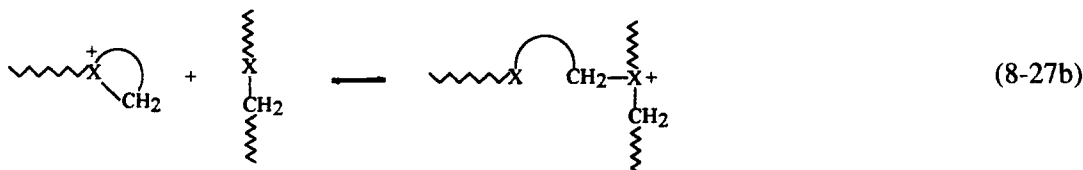
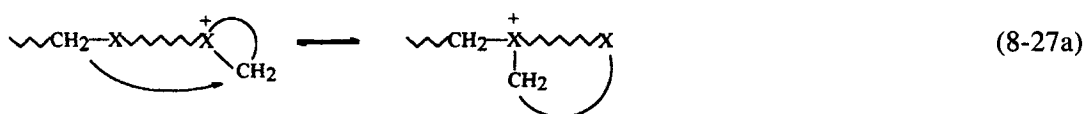
proportion depends on the solvent, on the type and nature of the onium ion, and, to a lesser extent, on the counterion. In polar solvents (nitromethane), the dissociation constants are relatively high and the proportion of free ions can be important (Ledwith and Sherrington, 1975; Matyjaszewski et al., 1979 a, b; Brzezinska et al., 1978). This allowed the measurement of their reactivity. Indeed kinetic studies performed on several heterocycles have shown that the absolute propagation rate constants of ion pairs and free ions are essentially the same. This is explained by weak electrostatic interactions in the ion pairs due to the relatively large size of the counterions, as well as by stronger solvation of the free cations by the monomer, which reduces their reactivity. Therefore onium ions may be considered as a unique entity which predominates in the polymer formation.

### 8.3.1.3 Chain Transfer to Polymer

In cationic heterocyclic polymerization, the electrophilic propagating species (onium ions) can react with the nucleophilic sites of the monomer and of the polymer chain, or with the counterion.

Reaction of onium ions with the monomer leads to chain propagation. As discussed earlier, monomer insertion is an equilibrated process. At low monomer concentrations or in the presence of large monomer rings, the reformation of monomer or other heterocycles of lesser ring strain may become predominant. These “depolymerization” and “back-biting” processes result from the reaction of polymer end groups with one heteroatom of their own chain to form a new onium ion [Eq. (8-27 a)]. They yield a series of heterocycles with their own polymerizability, which may react again with the onium ions to reform a linear poly-





mer. If the onium ions formed in these processes are unreactive, the reaction leads to termination.

A similar nucleophilic substitution may involve the onium ion of a chain end and nucleophilic sites located on another polymer chain [Eq. (8-27 b)]. Again, these reactions can be either reversible or irreversible. If the new oxonium ion formed is able to react with another heteroatom of the monomer or the chain, propagation and/or chain redistribution will occur. On the other hand, the formation of highly stabilized onium ions will result in a termination.

#### 8.3.1.4 Other Main Transfer and Termination Processes

In addition to the above reported reactions of active species with the nucleophilic sites of the chain, and provided that impurities are absent, the main other transfer and termination processes predominantly involve recombination with counterions.

Irreversible collapse of ionic species with the counterion is the most important termination process in heterocyclic cationic polymerization. Counterions with a pronounced nucleophilic character are able to successively compete with the monomer towards the active species and to form irreversibly (true termination) or reversibly (reversible termination) covalent terminals [Eq. (8-26)].

### 8.3.2 Main Families of Heterocyclic Monomers

After examination of the general features of heterocyclic monomer polymerization, the specific characteristics of the most important families of heterocycles (see Table 8-3) will be reviewed.

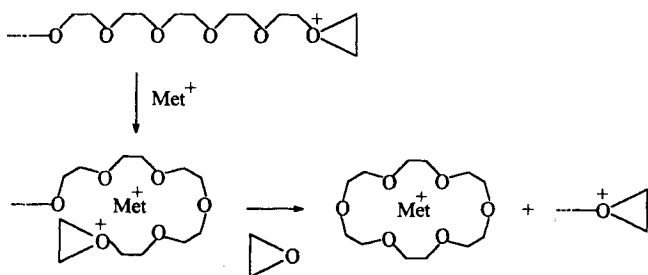
#### 8.3.2.1 Cyclic Ethers

The six-membered cyclic ethers do not polymerize due to the lack of ring strain, whereas the three- and four-membered rings, oxiranes and oxetanes, readily oligomerize.

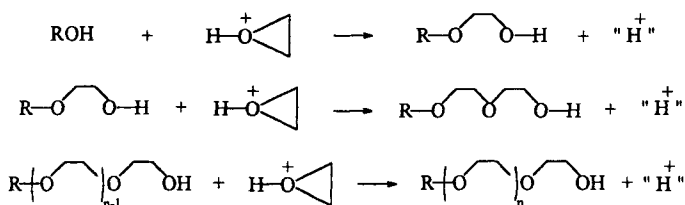
##### *Oxiranes*

In the presence of cationic initiators, ethylene oxide polymerization generally predominantly yields a cyclic dimer (dioxane) with a small fraction of oligomers ( $\bar{M}_n < 10^3 \text{ g mol}^{-1}$ ) (Kobayashi et al., 1979). This is due to the predominance of back-biting reactions when the active chain end mechanism is operating. This high tendency to form cyclics was exploited to prepare crown-ether derivatives (Scheme 8-10).

The proportion of cyclics is maximal when tertiary oxonium ions are the growing active species. When ethylene oxide polymerization is performed in the presence of hydroxy compounds, a different mecha-



Scheme 8-10.



Scheme 8-11.

nism, involving monomer activation, predominates. Under these conditions, the formation of linear oligomers is favored, whereas the amount of cyclics formed is minimized (Penczek et al., 1984; Penczek and Kubisa, 1993) (Scheme 8-11).

#### Oxetanes

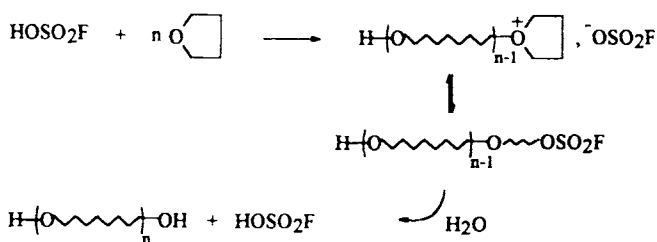
The polymerization of oxetane initiated by  $(C_2H_5)_3O^+$ ,  $PF_6^-$  yields poly(oxetane)s of rather low molar mass with broad molar mass distributions:  $\bar{M}_n = 35\,000\text{ g mol}^{-1}$  and  $\bar{M}_w/\bar{M}_n = 1.5-4$  (Black and Worsfold, 1976). Substitutions on the ring influence the ratio of linear polymer to cyclics. For example, 3-methyl-3-chloromethyloxetane leads to high molar mass polymers ( $\bar{M}_n = 76\,000\text{ g mol}^{-1}$  and  $\bar{M}_w/\bar{M}_n < 1.3$ ) in the presence of  $AlR_3 \cdot H_2O$  at  $20^\circ\text{C}$  (Aleksiuk et al., 1981).

#### Oxolanes

In this series, THF polymerization has been the most widely studied (Dreyfuss, 1982). Quantitative and fast initiation may be achieved with different initiators (typi-

cally  $CF_3SO_3H$ ). The main characteristic of the five-membered ring family is the slow reversibility of the propagation step. The latter is both governed by covalent esters and ionic species (Penczek and Matyjaszewski, 1976). For kinetic reasons, intramolecular chain transfer to the polymer (back-biting) is negligible during the polymerization, thus allowing the preparation of linear polymer without cyclics. The formation of the latter is only observed when the reaction mixture is kept for a long time without deactivation of the active chain ends. Since other side reactions (termination and transfer) are negligible, the cationic polymerization of THF may be considered as living. These characteristics enable the preparation of telechelics and block copolymers (with polyesters and polyamides) based on the poly(THF) backbone. An industrial route to  $\alpha,\omega$ -OH poly(THF) is depicted in Scheme 8-12.

Other routes leading to telechelic poly(THF), involving difunctional initiation, have also been described (Hofman et al., 1987).



Scheme 8-12.

### 8.3.2.2 Cyclic Acetals

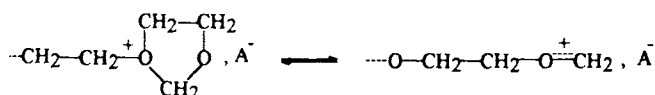
These monomers polymerize exclusively by cationic polymerization. Among the various cyclic acetals, 1,3-dioxolane and 1,3,5-trioxane have been the most widely studied. The latter yields polyoxymethylene, a polymer produced industrially.

#### 1,3-Dioxolane

In the presence of an electrophile, the abstraction of hydride from  $-\text{O}-\text{CH}_2-\text{O}-$  monomer units leads to the formation of carboxonium ions, which react with the monomer to finally form tertiary oxonium ions, the main propagating species [Eq. (8-21)]. The latter are in equilibrium with the corresponding carboxonium ions [Eq. (8-28)], which also contribute to the propagation reaction but to a lesser extent (Penczek and Szymanski, 1980).

Unlike THF polymerization, one main characteristic feature of the cationic polymerization of cyclic acetals is the important contribution of the polymer chains to transfer (Chwialkowska et al., 1982), leading, in particular, to the formation of cyclics during the polymerization.

The use of initiating systems with counteranions of very low nucleophilicity, such as  $\text{C}_6\text{H}_5\text{CO}^+\text{SbF}_6^-$ , enables, however, the preparation of living poly(1,3-dioxolane) (Kubisa and Penczek, 1978).



(8-28)

#### 1,3,5-Trioxane

Polyoxymethylene is industrially produced by the cationic polymerization of 1,3,5-trioxane. Typical initiators are  $\text{CF}_3\text{SO}_3\text{H}$  or  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ . Again, with this monomer the formation of cyclics by back-biting reactions does occur during the polymerization. Therefore a few percent of 1,3-dioxolane is generally added as comonomer to limit depropagation, which proceeds through the acetal ends. The latter process is stopped when a stable  $-\text{CH}_2-\text{CH}_2-\text{OH}$  group is present at the chain end.

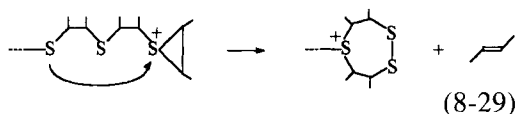
### 8.3.2.3 Cyclic Sulfides

Among the cyclic sulfides, three- and four-membered rings can be readily polymerized by cationic initiators. The polymerization equilibrium is shifted towards the formation of linear polymers.

#### Thiiranes

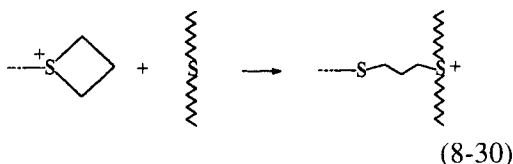
Similar to oxiranes, unsubstituted thiirane (ethylene sulfide) yields polymer of low molar mass, while mono- and disubstituted thiiranes can be converted into medium molar mass polysulfides. Intra- and intermolecular transfer processes to poly(alkyl sulfide) chains yield cyclics and branched polymer structures through the formation of sulfoni-

um ions (Simmons et al., 1979). In addition, the ability of the sulfur atoms of the chain to attack the sulfonium ions may also lead to isomerized products with disulfide bonds, as depicted in the case of dimethylthiirane polymerization in Eq. (8-29)



### Thietanes

The polymerization of thietanes is characterized by important transfer processes to polymer chains. The reaction mechanism [Eq. (8-30)], yielding branched macromolecular sulfonium ions, has been investigated in some detail by  $^1\text{H}$  NMR spectroscopy (Goethals and Drijvers, 1973).



Significant limitation of these transfer and termination reactions to polythietane chains can be achieved using substituted monomers. For example, in  $\text{CH}_2\text{Cl}_2$  at  $20^\circ\text{C}$ , 2,2-diethylthietane is converted quantitatively to a polymer while, under the same conditions, only 20% conversion can be achieved with thietane.

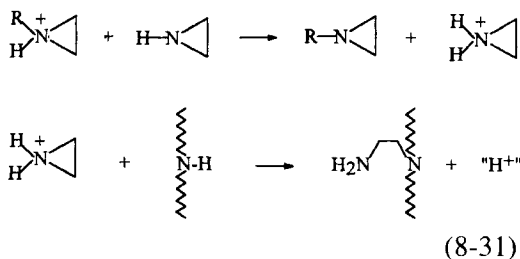
#### 8.3.2.4 Cyclic Amines

Most studies have dealt with the polymerization of three- and four-membered cyclic amines.

##### Aziridines

The polymerization of unsubstituted aziridine yields branched poly(ethylene imine)

due to the intermolecular formation of aziridinium ions (Dick and Ham, 1970 [Eq. (8-31)]).



Indeed, the synthesis of linear poly(ethylene imine) can only be achieved through indirect processes based on oxazoline polymerization. In the case of *N*-substituted aziridines with bulky groups, e.g., *N*-terbutylaziridine, chain transfer to the polymer is reduced and may even be suppressed. The polymerization of this last monomer is almost living, providing that alkylating agents such as triethyl oxonium salts are used as initiators (Goethals et al., 1977).

The controlled polymerization of *N*-terbutylaziridine enabled Goethals and co-workers to synthesize telechelics (Munir and Goethals, 1985), macromonomers (Goethals and Viegels, 1981), block copolymers (Goethals et al., 1984), and network (Van de Velde and Goethals, 1986) with a poly(*N*-terbutylaziridine) backbone.

##### Azetidines

The polymerization of these four-membered rings proceeds in a similar way and yields branched polyazetidines (Schacht and Goethals, 1974).

#### 8.3.2.5 Cyclic Esters

This section includes monomers like lactones, carbonates, anhydrides, orthoesters, etc.

### Lactones

A broad series of cationic initiating systems can be used to initiate the polymerization of four- and five-membered ring lactones. As a typical example,  $\text{RCO}^+$ ,  $\text{SbCl}_6^-$  initiates the polymerization of  $\beta$ -propiolactone giving high molar mass poly( $\beta$ -propiolactone) ( $\bar{M}_n = 3 \times 10^5 \text{ g mol}^{-1}$ ) with an experimental  $\text{DP}_n$  close to the theoretical value, whereas the formation of cyclic oligomers is not observed (Khomyakow and Lyudvig, 1971). In the case of lactone with a larger ring, transesterification and cyclization have to be considered (Ito et al., 1979): The cationic polymerization of lactones was applied to the preparation of macrocyclic esters that exhibit a selectivity for cation complexation (Tajima et al., 1981).

Cyclic fractions, on the other hand, can be drastically reduced when polymerization is performed in conditions where the activated monomer mechanism is predominant (Rosenberg, 1992).

### Glycolide

Cyclic dimers of  $\alpha$ -hydroxyacids, glycolide, or lactide yield high molar mass poly( $\alpha$ -hydroxyacid)s, which find applications as biodegradable materials (Vert et al., 1984). Usually their cationic polymerization is initiated by Lewis acids ( $\text{SbF}_3$ ,  $\text{ZnCl}_2$ ,

$\text{SnCl}_4$ , etc.), although the polymerization mechanism is still not well established.

### Cyclic Carbonates

The main characteristics of cyclic carbonate polymerization are very close to those observed for lactones. Moreover, some decarboxylation may take place under certain conditions, leading to the formation of ether units in the poly(carbonate) chains (Kricheldorf et al., 1992).

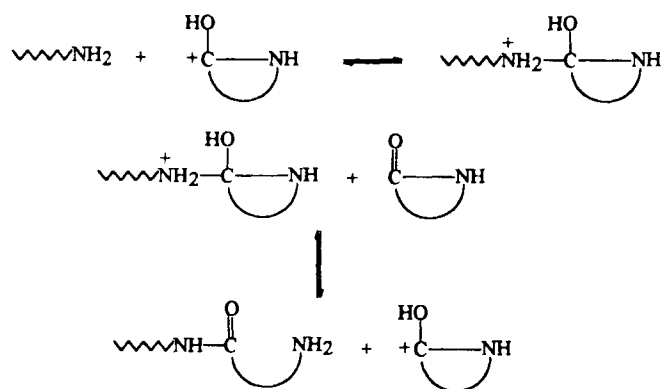
#### 8.3.2.6 Cyclic Amides

In addition to the polyaddition reaction, polyamides can be prepared by the anionic or cationic polymerization of lactams. Although the anionic process is preferred for unsubstituted lactams, in the case of *N*-substituted lactams the cationic approach is the only one possible.

As for other heterocyclics, the polymerization of unsubstituted lactams should preferably be performed by the activated monomer mechanism (Sebenda, 1988) (Scheme 8-13), since large amounts of cyclic oligomers are formed when the activated end mechanism is operating.

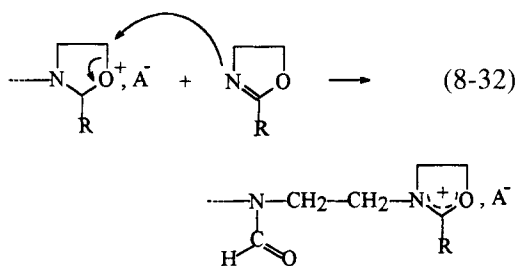
#### 8.3.2.7 Cyclic Iminoesters

A general, comprehensive review on the polymerization of cyclic iminoesters, name-



Scheme 8-13.

ly oxazolines, has recently been published (Aoi and Okada, 1996). Interestingly, the iminoester function of the monomer is transformed into an amido group during the polymerization. The proposed propagation mechanism is shown in Eq. (8-32). The six-membered ring oxazolines also polymerize, although they are not particularly strained: It is postulated that the conversion of the monomer iminoether group into an amido one is the driving force of the polymerization.



Since the formed amido group is stable and much less nucleophilic than the iminoester one, chain transfer to the polymer is nearly absent and the polymerization of oxazolines may exhibit a living character.

Recently, Kobayashi and co-workers prepared difunctional and star-shaped polyoxazolines ( $\bar{M}_n = 10\,000 \text{ g mol}^{-1}$  and  $\bar{M}_w/\bar{M}_n = 1.3$ ) using allylic and benzylic dihalides, as well as tetrahalides, as initiators (Kobayashi et al., 1992). Macromonomers, telechelics, and block copolymers of poly(oxazoline)s have also been prepared (Goethals et al., 1992, 1994, 1995).

### 8.3.2.8 Cyclic Phosphorous-Containing Compounds

Many cyclic phosphates have been reported to polymerize, including five- and six-membered rings (Lapienis and Penczek, 1984). The polymers issued from the ring-opening polymerization of cyclic pentavalent phosphorous-containing compounds are

interesting biopolymer mimics (nucleic acids).

The polymerization of cyclic compounds containing a trivalent phosphorous atom, including phosphites, phosphonites, and deoxophosphones, has also been studied.

Finally, it is worth mentioning in this section the cyclophosphazene monomers, which yield in the presence of Lewis acids inorganic synthetic polymers of specific physico-chemical properties (Horn and Kolmann, 1982).

### 8.3.2.9 Cyclic Silicone-Containing Compounds

#### *Cyclosiloxanes*

The polymerization of cyclic dimethylsiloxanes ( $D_3$  and  $D_4$  monomers, Table 8-3) is of great interest for the preparation of silicon materials and has been widely studied.

Although the anionic polymerization is easier to control, these monomers readily cationically and polymerize in the presence of protonic or Lewis acids. Trifluoromethanesulfonic acid or its derivatives are used as initiators (Gupta et al., 1993). Together with a linear, high molar mass polymer, cyclics are formed by back-biting.  $D_3$  polymerization is particular, since the presence of cyclic oligomers containing  $3n$  dimethylsiloxane units is only observed (Sigwalt et al., 1993). Their formation has been explained by a ring expansion polymerization mechanism and by the end-to-end ring closure of the growing polymer.

#### *Cyclosilanes*

The cationic ring-opening polymerization of strained cyclotetrasilanes yields inorganic polysilylenes with high molar masses. The best initiators are derivatives of tran-

sition metals (copper, palladium, platinum) (Cypryk et al., 1993).

### Cyclosilazanes

Polysilazanes have been widely studied by Soum and co-workers (Duguet et al., 1992, 1994; Duguet and Soum, 1995). The authors have demonstrated that linear, high molar mass polysilazanes can be obtained by the cationic ring-opening polymerization of cyclodisilazanes. These polymers are potential precursors to ceramic materials.

## 8.4 References

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## 9 Emulsion Polymerization

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## List of Symbols and Abbreviations

$C_i$	concentration of monomer $i$ in the polymer particles
$C_{i,\text{sat}}, C_{j,\text{sat}}$	saturation concentration of monomer $i/j$ in the polymer particles
$C_m$	monomer concentration in particles
$C_w^{\text{SAT}}$	saturation concentration of monomer in the waterphase
$f_{i,\text{d}}, f_{j,\text{d}}$	mole fraction of monomer $i/j$ in the monomer droplets
$f_{i,\text{p}}, f_{j,\text{p}}$	mole fraction of monomer $i/j$ in the polymer particles
$f_p$	volume fraction of polymer in particles
$F_s$	mole fraction of styrene in the copolymer
$\Delta G_a, \Delta G_c, \Delta G_d$	partial molar free energy of aqueous phase, colloidal phase, monomer droplets
$i, j$	monomer
$k$	rate coefficient of exit of radicals from particles
$k_p$	propagation rate coefficient
$k_t$	termination rate coefficient
$k_{tp}$	rate coefficient for bimolecular termination of radicals in particles
$M$	monomer
$[M]$	monomer concentration
$[M]_{\text{aq}}$	concentration of monomer in the aqueous phase
$[M]_{\text{aq},\text{sat}}$	the saturation concentration of monomer in the aqueous phase
$M_n$	number-average molecular weight
$M_w$	weight-average molecular weight
$M_z$	z-average molecular weight
$m_{ij}$	ratio of the molar volume of monomer $i$ over monomer $j$
$n$	number of radicals
$\bar{n}$	average number of radicals per particle
$N$	number of particles
$N_a$	Avogadro's number
$N_n$	number of particles containing $n$ radicals
$n_{m0}$	initially added number of moles of monomer per unit volume
$\bar{P}_n$	number average degree of polymerization of the polymer
$r$	reactivity ratio
$R$	gas constant
$r_0$	radius of unswollen micelles, vesicles, and/or polymer particles
$[R^*]$	radical concentration
$R_{\text{pol}}$	rate of polymerization
$s$	reactivity ratio
$t$	time
$T$	temperature
$v$	volume of a monomer-swollen particle
$V_m$	molar volume of monomer
$v_p$	volume fraction of polymer
$v_{d,i}, v_{d,j}$	volume fraction of monomers $i$ and $j$ in the monomer droplets
$v_{p,i}, v_{p,j}$	volume fraction of monomers $i$ and $j$ in the polymer particles

$W$	water
$x$	chain length, fractional conversion
$\gamma$	particle–water interfacial tension
$\rho_a$	rate coefficient of entry of free radicals
$\chi$	Flory–Huggins interaction parameter
$\chi_{i,j}$	Flory–Huggins interaction parameter between monomers $i$ and $j$
$\chi_{i,p}, \chi_{j,p}$	Flory–Huggins interaction parameter between monomers $i$ and $j$
ABS	acrylonitrile–butadiene–styrene
AMA	sodium di-hexyl sulfosuccinate
AOT	sodium di(2-ethylhexyl)sulfosuccinate
BA	butyl acrylate
BMA	butyl methacrylate
BMM-7-ON	<i>exo,exo</i> -2,3-bis(methoxymethyl)-7-oxanorbornene
CCD	chemical composition distribution
CMC	critical micelle concentration
CSTR	continuously stirred tank reactor
CTA	chain transfer agent
DA	dodecyl acrylate
DBSA	dodecylbenzene sulfonic acid
DMA	dodecyl methacrylate
DMF	dimethylformamide
DSC	differential scanning calorimetry
EHA	ethyl hexylacrylate
EMA	ethyl methacrylate
EPUE	explicit penultimate unit effect
EO	ethylene oxide
FID	flame ionization detection
HBMA	4-hydroxybutyl methacrylate
HEMA	2-hydroxyethyl methacrylate
HPLC	high performance liquid chromatography
HPMA	3-hydroxypropyl methacrylate
HUFT	Mansen–Ugelstack–Fitch–Tsai
IPUE	implicit penultimate unit effect
IUPAC	International Union of Pure and Applied Chemistry
MA	methyl acrylate
MAA	methacrylic acid
MM	molar mass
MMA	methyl methacrylate
MMCCD	molar mass chemical composition distribution
MMD	molar mass distribution
NMR	nuclear magnetic resonance
PAG	photoacid generator
PANI	polyaniline

PB	polybutadiene
PHA	poly-( <i>R</i> )-3-hydroxyalkanoate
PHB	poly-( <i>R</i> )-3-hydroxybutyrate
PLP–SEC	pulsed laser polymerization with size exclusion chromatography
PMOS	para methoxystyrene
PPC	pulsed packed column
PPy	polypyrrole
PSA	pressure-sensitive adhesive
PVAc	polyvinyl acetate
PCV	polyvinyl chloride
ROMP	ring-opening metathesis polymerization
S	styrene
SDS	sodium dodecyl sulfate
SEC	size exclusion chromatography
SEM	scanning electron microscopy
TEM	transmission electron microscopy
TFE	tetrafluoroethylene
THF	tetrahydrofuran
TLC	thin layer chromatography
UV	ultraviolet
VAc	vinyl acetate



## 9.1 Polymerization Techniques

A free-radical polymerization can be carried out using different techniques. Techniques most often used are bulk and solution polymerization where the monomer (a solvent) and the initiator are in one phase. The formed polymer remains soluble (either in the monomer or the solvent) until a high level of conversion is achieved. When the polymer precipitates from the continuous phase to form polymer particles which are not swollen with monomer, this is called precipitation polymerization. When the polymer particles swell with monomer, the technique is called dispersion polymerization, and as well as for polymerization in the continuous phase, the polymer particles are now also a locus of polymerization in contrast to the case for precipitation polymerization. Precipitation polymerization (Guyot, 1989) is often performed in aqueous media (for example, acrylonitrile polymerization in water).

Dispersion polymerization is usually performed in organic solvent, which are poor solvents for the formed polymer (Barrett, 1975). (Supercritical) liquid carbon dioxide ( $\text{CO}_2$ ) is used as a continuous medium for dispersion polymerization (Canelas et al. 1996). Suspension polymerization is polymerization in the monomer droplets; this is different from emulsion polymerization in that the initiator is oil-soluble and a nonmicelle forming stabilizing agent is used. PVC is manufactured using this technique.

The emulsion polymerization technique usually comprises a water-soluble initiator, a water-insoluble monomer, and a micelle-forming surfactant. The main locus of polymerization, in contrast to suspension polymerization, is the monomer-swollen latex. Therefore the term 'emulsion polymerization' is a misnomer; the starting point is an emulsion of monomer droplets in water, but

the product is a dispersion of polymer particles. A stable micro-emulsion of monomer droplets can also be formed (typical particle radius 10–30 nm), and a co-surfactant (e.g., hexanol) is usually applied. In micro-emulsion polymerization there is no longer a separate monomer phase (Holt, 1980; Guo et al., 1992). This is also the case in mini-emulsion polymerization, where the thermodynamically unstable droplets have a radius between 30 and 100 nm (Tang et al., 1992). It is also possible to perform inverse emulsion polymerizations, where the continuous phase is organic in combination with a water-soluble monomer (e.g., acrylamide; Vanderhoff et al., 1962).

## 9.2 Emulsion Polymerization

Emulsion polymerization involves the dispersion of monomers in a continuous aqueous phase and stabilization of this system by a surfactant. Usually, a water-soluble initiator is used to start the free-radical polymerization. This results in a reaction medium consisting of submicrometer polymer particles swollen with monomer and dispersed in an aqueous phase. The final product is called a latex and consists of a colloidal dispersion of polymer particles in water. Emulsion polymerization differs from suspension polymerization in the smaller size of the particles in which polymerization occurs, the applied stabilizing agents, the kind of initiator employed, and its mechanism and reaction characteristics. The emulsion polymerization process is often used for the (co)polymerization of monomers like vinyl acetate, ethylene, styrene, acrylonitrile, acrylates, and methacrylates. Also, conjugated dienes such as butadiene and isoprene are polymerized on a large industrial scale via the emulsion polymerization method. One of the advantages

of emulsion polymerization is the excellent heat exchange due to the low viscosity of the continuous phase during the whole reaction. Examples of applications are paints, coatings, glues, finishes, and floor polishes. Another important application is core-shell emulsion polymerization, i.e., the production of polymer particles with a layer structure. Core-shell products are used by the coating industry, in photo and printing materials, and especially in the production of high impact materials; in this case with a core of rubber and a shell of an engineering plastic.

By far the most important difference when compared with other polymerization techniques is the emulsion polymerization kinetics. Emulsion polymerization is unique in the sense that an increase in molar mass can be achieved without reducing the rate of polymerization. The molar mass and rate of polymerization can be varied independently over a large range. Emulsion polymerization is known for its relatively high rates of polymerization compared to other process strategies. A disadvantage of emulsion polymerization is the contamination of the polymer with surfactant and other additives. This is one of the obstacles for the breakthrough of latex paints, since the low molecular weight contaminants are often responsible for poor film-formation properties and water-sensitive paint films.

### 9.2.1 Mini- and Micro-Emulsion Polymerization

From a synthetic point of view, emulsion polymerization is not suitable for all monomers. For monomers that are highly water-soluble or, on the other hand, almost insoluble in water, the standard emulsion polymerization technique is not suitable (for the water solubilities of some monomers see

Appendix II). For water-soluble monomers, as well as in emulsion polymerization, aqueous phase polymerization can also occur.

In the case of highly water-soluble (e.g., acrylamide) or even water-miscible monomers (e.g., acrylic acid) inverse emulsion polymerization can be used. In inverse emulsion polymerization the continuous phase consists of an oil like kerosene or paraffin, in which water with dissolved monomer is emulsified, for example, with a high shear mixer like the Ultra Turrax in the presence of special emulsifiers (e.g., triblock copolymers). Polyacrylamide, used as a thickening agent in paints and a pushing fluid in tertiary oil recovery, is produced industrially by inverse emulsion polymerization.

In the case of monomers with low water-solubility another problem arises. In emulsion polymerization the transport of monomer from monomer droplets to the growing polymer particles is needed, and this demands a minimum water solubility of the monomer. For example, dodecylmethacrylate (water solubility 0.065 mmol/L) cannot be polymerized by emulsion polymerization, and even the polymerization kinetics of vinyl-2-ethylhexanoate with a reasonable water solubility (0.01 wt.% as compared to styrene with a water solubility of 0.03 wt.%) reflect some diffusion limitations for the transport of monomer (Kitzmler et al., 1995).

One solution to this problem is to directly polymerize in the monomer droplets which then have to be very small in order to keep the benefits of producing polymer in the form of a latex. As opposed to emulsion polymerization, where the droplets are the same size as those in suspension polymerization (1–10  $\mu\text{m}$ ), in mini- and micro-emulsion polymerization the droplets are very much smaller and enable the polymerization to commence in the monomer droplets.

In mini-emulsion polymerization the droplets are in the range of 50–500 nm in diameter. A mixed surfactant system comprising an ionic surfactant (e.g., SDS) and a cosurfactant (for example, a long chain alkane or alcohol) stabilizes the droplets, which are formed by a high shear field created by devices such as an ultrasonifier. The mini-emulsions are thermodynamically unstable and are therefore only stable for a limited period of time, ranging from hours to days.

In principle polymerization proceeds in the monomer droplets, and the final particle number is close to the initial number of monomer droplets. However, in many cases it turns out that not all the droplets are initiated to become polymer particles, but only a fraction ( $\leq 20\%$ ) of the initial number of monomer droplets. Miller et al. observed (1995) that the addition of pre-formed polymer greatly increases this fraction.

In micro-emulsions the droplets are even smaller (5–20 nm) and the micro-emulsion is thermodynamically stable. Also here, a mixed emulsifier system is used (Guo et al., 1992). As a result of the fact that in micro-emulsion polymerization the polymer particles are much smaller, monomer partitioning in copolymerizations is affected and special structures can be formed. Also, the apparent reactivity ratios can be different in micro-emulsion copolymerizations (Candau et al., 1986).

An interesting development is the use of phase transfer catalysts in order to increase the water solubility of monomers like dodecyl methacrylate and to facilitate normal emulsion polymerization for these monomers (Lau, 1996).

### 9.2.2 Basic Principles of Emulsion Polymerization

The physical picture of emulsion polymerization was based originally on the qualitative picture of Harkins (1947) and the quantitative treatment of Smith and Ewart (1948), with more recent contributions by Ugelstad and Hansen (1976), Gardon (1977 a, b), Gilbert and Napper (1974, 1975, 1977), Blackley (1975), Gilbert (1995), and Lovell and El-Aasser (1997). The main components of an emulsion polymerization recipe are the monomer(s), the dispersing medium (usually water), the surfactant (combination), and the initiator.

During the progress of the polymerization, three distinct intervals can be observed. Interval I is the initial stage, where particle formation takes place. Several mechanisms of particle nucleation have been proposed, which will be discussed in Sec. 9.2.3.

Interval II is characterized by a constancy of particle number, while polymerization in the particles proceeds in the presence of a separate monomer phase. The monomer-swollen particles grow at the expense of the monomer droplets. The beginning of interval II is usually taken as the point where the surfactant concentration drops below its critical micelle concentration. Interval III begins with the disappearance of monomer droplets, after which the monomer concentration in the particles and the water phase starts to decrease continuously.

### 9.2.3 Particle Nucleation

The nucleation stage constitutes so-called interval I in an emulsion polymerization, the initial period in which the particle number is changing due to particle formation. The consequence is that in the particle-formation period the rate of polymerization is not

constant but will increase to a maximum value. When this value is reached, particle formation is finished and, in the ideal situation, the number of polymer particles will stay constant, which is the start of interval II.

Particle nucleation in emulsion polymerization is a complex process which is still not well understood. Numerous investigations have been conducted in attempts to clarify this phenomenon. Harkins (1947) proposes the micelles in his widely used theory as the locus of nucleation (so-called micellar nucleation mechanism). Entry of a radical in a micelle produces a new polymer particle. As a result of compartmentalization of the radicals in the micellar phase and the resulting high radical concentration in the micelles and subsequent particles, the polymerization rate will be high in micelle and particle phases compared with the rate of polymerization in the monomer droplets. This nucleation mechanism is elegantly quantified by Smith and Ewart (1948) who stated that particle nucleation will stop when the surfactant concentration drops below its CMC due to the adsorption of surfactant onto the newly formed polymer particle surface. Systems of monomers with low water solubility (e.g., styrene) partially dissolved in micelles of a surfactant with low CMC and seemed to work well for such systems.

Although the Smith–Ewart nucleation model was successful for describing the styrene system, large deviations were observed for emulsion polymerization with other monomer systems, and in some cases when the surfactant concentration was varied from above the CMC to lower concentrations no discontinuity in, for example, particle number was observed. The situation became even more complex when it was shown that even without the use of a surfactant, stable polymer particles could be formed (El-Aasser and Fitch, 1987). Some important arguments against the Smith–Ewart nucleation model are: Particles are formed even when no micelles are present, more water-soluble monomers do not fit the theory, and a maximum in the polymerization rate at the end of the nucleation period is predicted but has rarely been observed.

These observations called for alternative models of nucleation (Willes, 1949; Goodwin et al., 1973, 1974, 1978; Munro et al., 1979; Goodall et al., 1977; Song and Poehlein, 1989). A homogeneous nucleation model was proposed (Goodall et al., 1977; Fitch and Tsai, 1971) in which radicals react in the aqueous phase with solubilized monomer to form growing oligomeric species. These species will form particles when the critical water solubility length is reached. The consequence is that the water solubility of the monomer, the initiator concentration, and the water solubility of the initiator are crucial parameters in the emulsion polymerization process. The formation of primary particles is described by the homogeneous nucleation theory of Fitch and Tsai (1971), and is known as the HUFT theory (Hansen–Ugelstad–Fitch–Tsai), which implies that precursor particles are formed in the aqueous phase by precipitation of oligomeric radicals above a critical chain length. No particles are nucleated before the oligomer radicals have reached a critical chain

**Table 9-1.** Comparison of surface area between monomer droplets, micelles, and polymer particles.

	Monomer droplets	Micelles	Polymer particles
Number ( $\text{ml}^{-1}$ )	$10^7$	$10^{18}$	$10^{15}$
Diameter (nm)	$10^5$	10	100
Surface area ( $\text{m}^2 \text{ml}^{-1}$ )	0.314	314	31

length  $x$ , and this will take some time. The precipitation of precursor particles is in fact a thermodynamic effect.

Feeney et al. (1984) proposed a refinement of this theory in which it is assumed that initially colloidally unstable precursor particles are formed as a result of the previously described growth of oligomers in the aqueous phase; these particles will precipitate after reaching a critical length and then coagulate with each other and with mature particles to form growing polymer particles. Precursor particles may coagulate with *other* precursor particles. Eventually the size of the coagulated entities becomes large enough to allow appreciable monomer swelling to occur by excluding water, i.e., the monomer concentration in the particles increases. Thereafter, the coagulated entity is considered to be a stable polymer particle which may grow more rapidly due to higher monomer concentration and lower radical loss. The coagulation events involved in the nucleation mechanism explain the maximum in the particle numbers in interval I for systems without or with low surfactant content. Recently, new insights (Gilbert et al., 1992; Hansen, 1992) and the quantification of nucleation models have revealed that in most cases micellar and homogeneous nucleation occur concurrently, which is also intuitively more acceptable. Tauer and Kühn (Tauer and Kühn, 1995; Kühn and Tauer, 1996) used the classical nucleation theory in combination with the Flory–Huggins theory of polymer solutions to explain the particle formation process. The difference with the homogeneous coagulative nucleation model is the definition of the time period in which nucleation takes place. It is very difficult to discriminate between these models on the basis of experimental data.

In conclusion, the determination of the nucleation mechanisms operative in a given

polymerization system is very difficult. The reason is that there is no general nucleation mechanism that can describe all the aspects of a given polymerization system. Thus the nucleation mechanism is dependent upon the emulsion polymerization system characteristics. These characteristics are the type of monomer, the type of initiator, the temperature, the importance of aqueous phase kinetics, the water solubility of the monomer and the initiator, the propagation rate constant, etc. However, the emulsion polymerization system can be divided into two categories: systems starting from surfactant concentrations above the CMC, and systems with surfactant concentrations below the CMC, including the surfactant-free systems. For these two options some general conclusions can be drawn (Casey et al., 1993):

– Nucleation mechanism below the CMC: In an emulsion polymerization where the amount of surfactant is below the CMC of the surfactant, there are no micelles present. The most likely nucleation mechanism will then be homogeneous nucleation. However, due to the aqueous phase kinetics, termination products are formed (dead products). These termination products may adsorb upon the polymer particles if their chain lengths are larger than their critical chain length. In addition, the moieties may act as in situ formed surfactant, stabilizing the polymer particles. The in situ formed surfactant, if its concentration is high enough, may reach its CMC. The final conclusion is that the dominant nucleation mechanism for polymerization systems below the CMC is the homogeneous coagulative mechanism, although micellar nucleation cannot always be completely ruled out.

– Nucleation mechanism above the CMC: The nucleation mechanism in (commercial) emulsion polymerization processes above the CMC is usually very complex, because

then micelles are also present. It can simultaneously involve all three types of nucleation processes (Morrison et al., 1992); however, the mechanism of micellar nucleation often dominates. When micelles are present, aqueous phase propagation continues only until an oligomer becomes surface active. Particle formation takes place when a surface-active z-mer enters a micelle by picking up sufficient additional conventional surfactant. Coagulation of newly formed particles also takes place. Particle formation stops when the number of particles is sufficient to capture all new radicals. A complete mathematical model that combines the different mechanisms has not yet been developed, and it is seen as an important task for the future (Gilbert, 1995).

### 9.2.4 Particle Growth

Once formed and given colloidal stability, the particles will take part in the polymerization process in intervals I, II, and III. The kinetics are mainly controlled by the distribution and exchange of radicals over the various phases and cannot be oversimplified. Models are numerous but well described in excellent reviews (Ugelstad and Hansen, 1976; Hansen and Ugelstad, 1982; Gilbert, 1995; Gilbert and Napper, 1983). The basic rate equation for homogeneous batch free radical polymerization is

$$R_{\text{pol}} = -\frac{d[M]}{dt} = k_p[M][R^*] \quad (9-1)$$

where  $R_{\text{pol}}$  is the rate of polymerization per unit volume,  $k_p$  the propagation rate coefficient,  $[M]$  the monomer concentration, and  $[R^*]$  the radical concentration. In the emulsion polymerization process the main loci of polymerization are the particles; thus the rate equation must contain the number of particles,  $N$ , as well as the concentration of monomer and radicals in the particles, lead-

ing to

$$R_p = \frac{k_p \bar{n} C_m N}{N_a} \quad (9-2)$$

where  $C_m$  is the monomer concentration in the particles,  $\bar{n}$  is the average number of radicals per particle, and  $N_a$  is Avogadro's number. The time evolution of the fractional conversion in a batch process,  $x$  is then

$$\frac{dx}{dt} = \frac{k_p C_m N}{N_a n_{m0}} \bar{n} = A \bar{n} \quad (9-3)$$

where  $A = k_p C_m N / N_a n_{m0}$  and  $n_{m0}$  is the initially added number of moles of monomer per unit volume. Equation (9-3) is valid for intervals II and III, and, for interval I,  $N$  and  $C_m$  should be replaced by  $N(t)$  and  $C_m(t)$ , respectively. In interval II,  $k_p$  and  $C_m$  are constant at least to within an excellent approximation. The  $k_p$  of several types of monomer is given in Appendix I.

The value of  $\bar{n}$  (the average number of radicals per particle) is determined by three processes, namely

- 1) absorption of radicals from the water phase into particles;
- 2) desorption of radicals from particles; and
- 3) bimolecular termination of radicals in the particles.

Smith and Ewart (1948) were the first at formulating an equation for  $\bar{n}$  in the form of a set of population balance equations describing the number of particles  $N_n$  containing  $n$  radicals

$$\begin{aligned} \frac{dN_n}{dt} = & \frac{\rho_a}{N} (N_{n-1} - N_n) \\ & + k [(n+1) N_{n+1} - n N_n] + \frac{k_{tp}}{v} \\ & + [(n+2)(n+1) N_{n+2} - n(n-1) N_n] \end{aligned} \quad (9-4)$$

where  $\rho_a$  is the rate coefficient of entry of free radicals,  $k$  is the rate coefficient of exit of radicals from particles,  $k_{tp}$  is the rate coefficient for bimolecular termination of

radicals in the particles, and  $v$  the volume of a monomer-swollen particle. Several workers have reported various ways of solving this general set of equations. Smith and Ewart presented very useful solutions for three limiting cases determined by the ratios of entry, exit, and termination:

Case I:  $(\rho_a/N) \ll k: \bar{n} \ll 0.5$

This situation is the result of faster desorption than absorption of radicals by particles. Consequently, particles contain at most one radical at a time and on average a number far smaller than unity. On neglecting the extremely few particles with more than one radical, Eq. (9-4) simplifies to

$$\frac{dN_0}{dt} = -N_0 \frac{\rho_a}{N} + N_1 k \quad (9-5)$$

As in this case there will be far more  $N_0$  particles as compared to  $N_1$  particles, it follows that  $N_0 \approx N$ , leading to

$$\frac{\rho_a}{kN} = \frac{N_1}{N} = \bar{n} \quad (9-6)$$

Case II:  $k \ll (\rho_a/N) \ll (k_{tp}/v): \bar{n} = 0.5$

This situation is the result of instantaneous termination when a second radical enters a particle already containing a radical, and with negligible desorption of radicals from particles. The time interval between entries varies in a random fashion. When a radical enters a particle, this particle immediately starts to polymerize at a steady state rate. As soon as a second radical enters, this rate abruptly falls to zero. Under these conditions it is obvious that on average the active and inactive periods of each particle are equal in length, so that  $N_0 = N_1$  and  $N_1/N = \bar{n} = 0.5$  ( $N = N_0 + N_1$ ). Case I and II are known as zero-one systems. Note that without careful examination, it cannot be presumed that an emulsion system can be described with case II approximations.

Case III:  $(k_{tp}/v) \ll (\rho_a/N): \bar{n} \gg 0.5$

This situation occurs when bimolecular termination is no longer instantaneous upon entry of a second radical in an active particle. Smith and Ewart neglected radical exit in their treatment of this case. With a sufficiently large  $\bar{n}$ , the steady state condition is  $\rho_a/N = 2k_{tp}\bar{n}^2/v$ . Since the total volume of polymer per unit volume of aqueous phase is  $V = N \times v$ , the rate of polymerization becomes

$$R_{pol} = k_p C_m (\rho_a V / 2k_t)^{0.5} \quad (9-7)$$

Ugelstad et al. (1967) extended the general equation Eq. (9-4), to include aqueous phase kinetics. Gilbert and Napper have contributed and still contribute important work in this field. They were the first to present a general solution to Eq. (9-4) using modern numerical techniques (Gilbert and Napper, 1989) and re-examination of the Smith-Ewart cases. In their treatment of the zero-one equations, termination is instantaneous and therefore not rate-determining. As a consequence, only entry and exit of radicals are taken into account.

### 9.2.5 Molar Mass and Molar Mass Distribution

In the case of a homopolymer molecule, the most important characteristic is its size or molar mass. The molar mass (defined by various averages and especially the molar mass distribution) determines a large range of properties of the polymer material. Naturally this applies to copolymers as well, in which case the chemical composition distribution also plays an important role.

The molar mass (MM) and its distribution (MMD) can be measured in many ways. For definitions of MM averages see Young and Lovell (1991). A distinction can be made between absolute, relative, and equivalent

methods, and also between the particular average (number-average  $M_n$  or weight-average  $M_w$ , or higher averages like the z-average) or distribution resulting from these methods. Absolute methods give the MM without the need of calibration by other methods. Relative methods require a calibration relationship between the quantity measured and the MM. Equivalent methods (like end-group titration giving  $M_n$ ) require knowledge about the chemical structure of the compound. Absolute methods include osmometry ( $M_n$ ), ebullioscopy ( $M_n$ ), cryoscopy ( $M_n$ ), light scattering ( $M_w$ ), and ultracentrifugation ( $M_n$ ,  $M_z$ ). Viscometry (viscosity average MM), size exclusion chromatography (MMD), and field-flow fractionation (MMD) are relative methods. These methods also differ in the range of MM that can be analyzed. A short overview has been given by Springer et al. (1992) and a more extensive overview can be found in Hunt and James (1993).

In particular, in an emulsion polymerization the MMD is determined by the events that can start, continue, or stop the growth of a polymer chain. These events are entry of a radical in a particle, propagation, and termination. Considering termination, we can distinguish two types of chain-stopping process bimolecular termination and transfer of the free-radical activity of the chain end to another molecule. Bimolecular termination can occur through disproportionation or combination. Transfer can occur to transfer agents, deliberately added, or to components present in the recipe (e.g., surfactant, initiator, monomer, polymer). In particular, in emulsion polymerization transfer to monomer is a very important chain-stopping process because it generates a small radical that can also exit the polymer particle.

Theories to predict the MMD in emulsion polymerization have been developed by

several groups (Tobita et al., 1994; Giannetti et al., 1988a; Lichti et al., 1982).

### 9.2.6 Particle Size Distribution

If the polymer produced by an emulsion polymerization is applied in the form of a latex, the particle size distribution is an additional factor that determines the properties of the latex. For example, latex rheology, film formation of a latex paint, light scattering, and the appearance of a coating are influenced by the particle size and the particle size distribution. There are many techniques for the measurement of average particle size and particle size distribution. No single technique is universally applicable and each one can address its own range of particle sizes. Transmission electron microscopy is one of the more reliable techniques, although even with this technique artifacts can occur, for example, if the polymer particles are soft and change their shape during analysis. Other techniques are static and dynamic light scattering, ultracentrifugation, capillary hydrodynamic fractionation, field-flow fractionation, disk centrifuge, and the coulter counter technique. A review of these techniques is given in Hunter (1993).

Models to predict particle size distributions not only have to account for particle nucleation and growth (Gilbert, 1995), but partial coagulation or coalescence during the emulsion polymerization sometimes also has to be taken into account (Weerts et al., 1991).

### 9.2.7 Ingredients in Recipes

In this and the following sections an overview is given of the major ingredients in emulsion polymerization. A laboratory scale recipe for an emulsion polymerization



contains monomer, water, initiator, surfactant, and sometimes a buffer and/or chain transfer agents. The commercial emulsion polymerization recipes are rather complicated, rather indistinct, and for one specific application only. Small changes in recipe or reaction conditions often result in unacceptable changes in the quality of the product formed. These recipes may contain 20 or more ingredients, such as water, monomer (and comonomers), surfactant (often a mixture), initiation system, additives (electrolytes, pH controller, chain transfer agents (often a mixture), sequestering agents, and contaminants from chemicals and from corrosion.

### 9.2.7.1 Monomers

The monomers used in an emulsion polymerization must have at least a minimum, but also a limited solubility in water and swell its product polymer. The most common monomers are styrene, butadiene, vinylacetate, acrylates and methacrylates, acrylic acid, and vinyl chloride. More types of monomer are listed in the tables of Appendices I and II.

### 9.2.7.2 Initiators

The most commonly used laboratory and industrial water-soluble initiators are potassium, sodium, and ammonium salts of persulfate. Next in line are the water soluble azo-compounds, especially those with an ionic group, such as 2,2'-azobis(2-amino-propane)dihydrochloride.

Above pH 6 and a temperature of 50°C, persulfate dissociates at the O–O bond by which two identical radicals are formed:  $S_2O_8^{2-} \rightarrow 2SO_4^{\cdot-}$ . Strong evidence suggests water molecules play a role in the dissociation to form  $HSO_4^{\cdot-}$ , which lowers the pH. Therefore a buffer is necessary to control the pH and thus the efficiency of the initiator.

When the polymerization should be performed at lower temperatures (less than 50°C), a redox system can be used. A lower polymerization temperature has the advantage of reducing chain branching and crosslinking in the synthesis of rubbers; a typical example of a redox systems is Fe(II) and cumene hydroperoxide.

There are also other methods to create free radicals such as  $\gamma$ -radiolysis, UV, and laser in combination with photoinitiators, and electron beam techniques.

### 9.2.7.3 Surfactants

A surfactant [(**surface active agent**) also referred to as an emulsifier, soap, or stabilizer] is a molecule with both hydrophilic and hydrophobic segments. The general name for this group is amphiphatic molecules, indicating their tendency to arrange themselves at oil–water interfaces. In emulsion polymerization, surfactants serve three important purposes: stabilization of the monomer droplets, generation of micelles, and stabilization of the growing polymer particles leading to a stable end product.

As mentioned earlier, a surfactant molecule consists of a (polar) hydrophilic and a (apolar) hydrophobic segment. Surfactants are mostly classified according to the hydrophilic group:

- anionic surfactants, where the hydrophilic part is an anion,
- cationic surfactants, where the hydrophilic part is a cation,
- amphoteric surfactants, where the properties of the hydrophilic function depend on the pH,
- nonionic surfactants, where the hydrophilic part is a nonionic component, for instance, polyols, sugar derivatives, or chains of ethylene oxide.

Other types of surfactant are the polymeric (steric) stabilizers, such as partially hydrolyzed polyvinyl acetate. Also the oligomeric species formed in situ, when  $\text{SO}_4^{\cdot-}$  radicals react with some monomer units in the aqueous phase, will have surface active properties, and can even form a colloidally stable latex (El-Aasser and Fitch, 1987).

Important technical emulsifiers are fatty alcohol–ethylene oxide (EO) adducts as well as nonylphenol–EO adducts. The most commonly used anionic surfactants are sodium dodecyl sulfate (SDS) and the aerosol series (sodium dialkyl sulfosuccinates), such as aerosol OT [AOT, sodium di(2-ethylhexyl)sulfosuccinate] and aerosol MA (AMA, sodium di-hexyl sulfosuccinate). These surfactants are often used when monodispersed latices are required, due to their high critical micelle concentration (CMC) and a relatively large aggregation number (number of surfactant molecules per micelle).

#### 9.2.7.4 Others

**Electrolytes:** These are added for several reasons. For example, they can control the pH, which prevents hydrolysis of the surfactant and maintains the efficiency of the initiator. Electrolytes can induce particle size monodispersity and also particle coagulation.

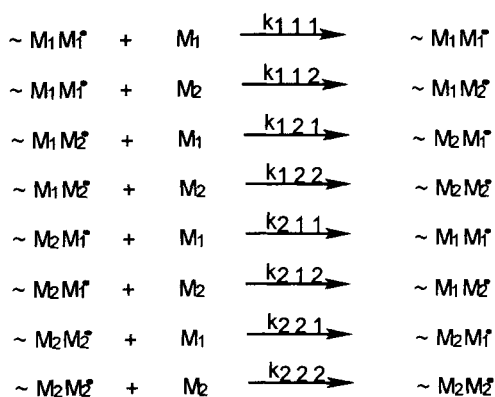
**Chain transfer agents:** Emulsion polymerization often results in an impractically high molecular mass polymer. Therefore, to moderate the molar mass, chain transfer agents (CTAs), usually mercaptans, are frequently used. The mercaptan is introduced into the reactor together with the monomer phase. The consumption of the mercaptan taking place in the loci should be properly kept in balance with monomer consumption.

## 9.3 Emulsion Copolymerization

### 9.3.1 Penultimate Unit Effect in Copolymerization

In the usual copolymerization approach, four propagation reactions are distinguished. Two different radical chain ends can react with two different monomers. The model that describes this kind of copolymerization is referred to as the terminal model, or the Mayo–Lewis model. In the majority of cases, this approach appears to be insufficient to describe the copolymerization kinetics. In a relatively small number of cases this approach fails to describe the copolymer composition and the monomer sequence distribution. In order to provide a good description of the systems that do not obey the terminal model, a large variety of models has been proposed in the past. The model that received the most attention is an extension of the terminal model. Instead of taking only the terminal monomer unit into account with respect to the reactivity of a chain end radical, the second to last (penultimate) monomer unit is also considered important (Fukuda, 1992).

The penultimate unit model uses eight different propagation reactions, i.e., four different chain ends and two different monomers. The propagation reactions in the penultimate unit model are represented in Scheme 9-1.



Scheme 9-1

In case of the penultimate unit model, the reactivity ratios are defined as follows

$$r_{11} = \frac{k_{111}}{k_{112}}, \quad r_{21} = \frac{k_{221}}{k_{212}}$$

$$r_{12} = \frac{k_{122}}{k_{121}}, \quad r_{22} = \frac{k_{222}}{k_{221}}$$

$$s_1 = \frac{k_{211}}{k_{111}}, \quad s_2 = \frac{k_{122}}{k_{222}}$$

It is easy to understand that the terminal model is a special case of the penultimate unit model, i.e., when  $r_{11}=r_{21}$ ,  $r_{12}=r_{22}$ , and  $s_1=s_2=1$ .

It has been known for a long time that the copolymerization of styrene and acrylonitrile does not obey the terminal model (Hill, 1982). Copolymer composition and monomer sequence distribution require the use of the penultimate unit model for an adequate description. This type of behavior, according to the penultimate unit model, is the classical case; here only the  $r_{ij}$  reactivity ratios are considered and it is called the explicit penultimate unit effect (EPUE) because of the introduction of the  $s_i$  reactivity ratios (Fukuda, 1991). This in contrast to the implicit penultimate unit effect (IPUE) where copolymer composition and monomer sequence distribution are adequately described by the terminal model, but  $k_p$  deviates from the terminal model. The deviation of  $k_p$  from the terminal model is accounted for by  $s_i$  values that are not equal to unity. This means that the penultimate unit affects the rate of the homopropagation reaction. Typical examples of copolymerizations that exhibit an IPUE and an EPUE are shown in Tables 9-2 and 9-3, respectively.

In terms of emulsion copolymerization, the IPUE will only affect the rate of copolymerization compared to the prediction based on the terminal model. The EPUE on the other hand will influence the copolym-

**Table 9-2.** Reactivity ratios of copolymerizations with an IPUE.

Monomer 1/monomer 2	$r_1$	$r_2$	$s_1$	$s_2$
Styrene/methyl methacrylate <sup>a</sup>	0.47	0.45	0.43	0.16
Styrene/methyl acrylate <sup>b</sup>	0.73	0.19	0.59	0.02

<sup>a</sup> Davis (1989); <sup>b</sup> Schoonbrood (1994).

**Table 9-3.** Reactivity ratios of copolymerizations with an EPUE.

Monomer 1/monomer 2	$r_{11}$	$r_{21}$	$r_{12}$	$r_{22}$
Styrene/acrylonitrile <sup>a</sup>	0.250	0.604	0.105	0.070
Styrene/maleic anhydride (DMF) <sup>b</sup>	0.018	0.046	0	0

<sup>a</sup> Klumperman and Kraeger (1994); <sup>b</sup> Klumperman and Vonk (1994).

er composition and the microstructure, as in the earlier mentioned copolymerization of styrene and acrylonitrile. This copolymerization is carried out in emulsion on a large scale, i.e., for the synthesis of ABS the copolymerization of styrene and acrylonitrile is carried out in the presence of a polybutadiene seed latex. This results in the production of a rubber-modified material with interesting properties.

### 9.3.2 Monomer Partitioning in Emulsion Polymerization

As a result of the intrinsic heterogeneity of an emulsion polymerization system, the kinetics and mechanisms which control this polymerization are difficult to describe. In order to get more insight into the kinetic processes involved in an emulsion (co)polymerization, a detailed knowledge of the partitioning of monomer(s) over the different phases present is necessary. The monomer concentration in the polymer particles di-

rectly determines the rate of polymerization, while the monomer ratio in the polymer particles determines the chemical composition of the copolymer formed (see also Sec. 9.3.1, 9.3.3, and 9.3.4). Therefore accurate knowledge of the concentration of the monomer in the different phases of the polymerization system is necessary to develop and test kinetic models for the emulsion polymerization process. These models can be useful in the design of polymerization reactors, process control, and product characteristics, such as molar mass and chemical composition distributions of the copolymers formed. In this section, a thermodynamic model based on the Flory–Huggins theory (Flory, 1953) of polymer solutions will be discussed and applied to experimental results on the partitioning of monomer(s) over the different phases present during an emulsion (co)polymerization. The dynamics of swelling depend on the particle size; but not on the absolute concentration, as will be discussed in this paragraph.

At equilibrium the partial molar free energy of the monomer will be equal in each of the phases present, i.e., the monomer-swollen colloid (micelles, vesicles, and/or polymer particles), the monomer droplets, and the aqueous phase (Morton et al., 1954; Ugelstad, 1983; Gardon, 1968)

$$\Delta G_c = \Delta G_d = \Delta G_a \quad (9-8)$$

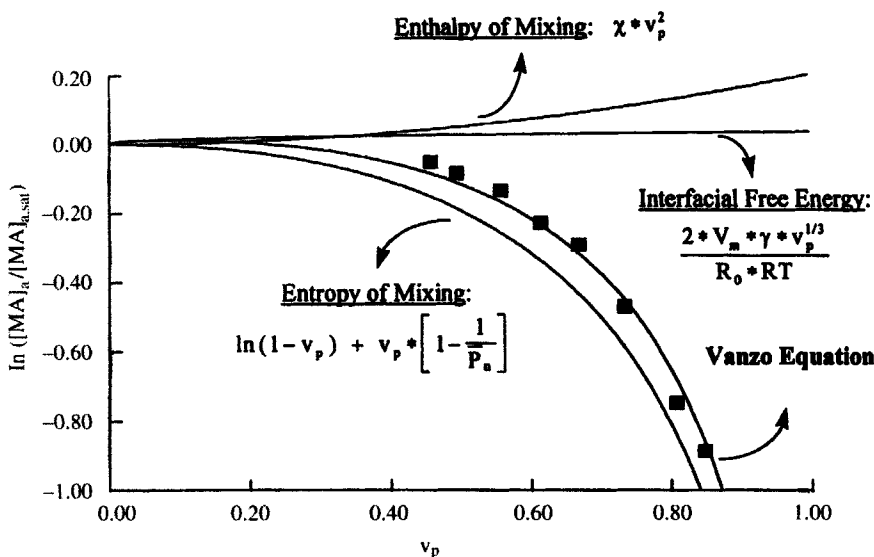
where  $\Delta G_c$ ,  $\Delta G_d$ , and  $\Delta G_a$  are the partial molar free energies of the colloidal phase, the monomer droplets, and the aqueous phase, respectively. Utilizing the appropriate equations for the partial molar free energy of the colloidal and aqueous phase [see, for derivation, e.g., Maxwell et al. (1992a)], Eq. (9-9) can be obtained, also known as the Vanzo equation (Vanzo et al., 1965), which describes the partitioning of monomer between the aqueous phase and the polymer particles in the absence of, in general,

monomer droplets

$$\ln(1 - v_p) + v_p \left(1 - \frac{1}{\bar{P}_n}\right) + \chi v_p^2 + \frac{2 V_m \gamma v_p^{1/3}}{r_0 RT} = \ln \left( \frac{[M]_{aq}}{[M]_{aq,sat}} \right) \quad (9-9)$$

where  $v_p$  is the volume fraction of polymer,  $\bar{P}_n$  is the number average degree of polymerization of the polymer,  $\chi$  is the Flory–Huggins interaction parameter between the monomer and the polymer, while  $R$  is the gas constant, and  $T$  the temperature.  $V_m$  is the molar volume of the monomer,  $\gamma$  is the particle–water interfacial tension, and  $r_0$  is the radius of the unswollen micelles, vesicles, and/or polymer particles.  $[M]_{aq}$  is the concentration of monomer in the aqueous phase and  $[M]_{aq,sat}$  the saturation concentration of monomer in the aqueous phase. Figure 9-1 shows the contributions of the different terms of Eq. (9-9) to the Vanzo equation.

The partitioning of monomer between the aqueous phase and the polymer particles, below and at saturation, can be predicted by Eq. (9-9). However, this requires both the Flory–Huggins interaction parameter and the interfacial tension to be known. These parameters may be polymer volume fraction dependent [see Maxwell et al. (1992a, b) for prediction of monomer partitioning]. Equations similar to Eq. (9-9) can be derived for the swelling of micelles and vesicles with one or more monomers, and of homopolymer, co- and terpolymer polymer particles with two or more monomers at and below saturation (Noel et al., 1993; Schoonbrood et al., 1994). Here we will discuss two typical examples: the swelling behavior of poly(styrene-*co*-methyl methacrylate) and polybutadiene-*graft*-poly(styrene-*co*-methyl methacrylate) polymer particles with styrene and methyl methacrylate (Aerdts et al., 1993).



**Figure 9-1.** Comparison of theoretical predictions and experimental measurements of methyl acrylate partitioning at 45 °C for a polymethyl acrylate seed latex with an unswollen radius of 91 nm (closed squares). Theoretical predictions: Different terms of Eq. (9-9) are depicted for the Vanzo equation:  $\chi=0.2$  and  $\gamma=45$  mN/m were taken from literature (Maxwell et al., 1992a).

An expression was derived earlier that can describe the swelling behavior of a polymer particle with one monomer below and at saturation. In the case of saturation swelling with two monomers, substituting the appropriate expression for the partial molar free energy of the different phases into Eq. (9-8), Eq. (9-10) for monomer  $i$  can be obtained [for exact derivation see, e.g., Maxwell et al. (1992a, b) and Noel et al. (1993)], which is quite similar to Eq. (9-9)

$$\begin{aligned}
 & \ln v_{p,i} + (1 - m_{ij}) v_{p,j} + v_p + \chi_{ij} v_{p,i}^2 + \chi_{ip} v_p^2 + \\
 & + v_{p,j} v_p (\chi_{ij} + \chi_{ip} - \chi_{jp} m_{ij}) + \\
 & + \frac{2 V_{m,i} \gamma v_p^{1/3}}{r_0 R T} \\
 & = \ln v_{d,i} + (1 - m_{ij}) v_{d,j} + \chi_{ij} v_{d,i}^2 \\
 & = \ln \left( \frac{[M_i]_{aq}}{[M_i]_{aq,sat}} \right) \quad (9-10)
 \end{aligned}$$

where  $v_{p,i}$  and  $v_{p,j}$  are the volume fractions of monomers  $i$  and  $j$  in the polymer particles, respectively.  $\chi_{i,j}$  is the Flory–Huggins

interaction parameter between monomers  $i$  and  $j$ , while  $\chi_{i,p}$  and  $\chi_{j,p}$  are the Flory–Huggins interaction parameters between monomers  $i$  and  $j$  and the polymer, respectively,  $m_{ij}$  is the ratio of the molar volume of monomer  $i$  over monomer  $j$ , and  $v_{d,i}$  and  $v_{d,j}$  represent the volume fraction of monomers  $i$  and  $j$ , respectively, in the monomer droplets. It can be shown from Eq. (9-10) that, at saturation swelling, the mole fraction of monomer  $i$  in the monomer droplets ( $f_{i,d}$ ) is equal to the mole fraction of monomer  $i$  in the polymer particles ( $f_{i,p}$ ). This also holds for monomer  $j$ . This is envisaged in Eq. (9-11) (Maxwell et al., 1992b)

$$f_{i,p} = f_{i,d} \quad \text{and} \quad f_{j,p} = f_{j,d} \quad (9-11)$$

where  $f_{j,d}$  and  $f_{j,p}$  are the mole fractions of monomer  $j$  in the monomer droplets and in the polymer particles, respectively. Making the assumption that the total monomer concentration in the polymer particles is equal to the sum of the concentrations of the individual monomers, together with Eq. (9-11)

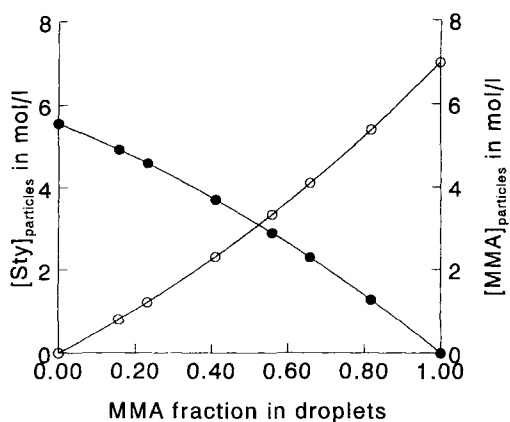
the concentration of monomer  $i$  in the polymer particles can be predicted from the individual saturation concentrations of monomers  $i$  and  $j$  in the polymer particles, i.e.,  $C_{i,\text{sat}}$  and  $C_{j,\text{sat}}$ , respectively. For a given seed latex, the concentration of monomer  $i$  in the polymer particles ( $C_i$ ) is related to the mole fraction of monomer  $i$  in the monomer droplets ( $f_{i,d}$ ) and given by the following equation (Maxwell et al., 1992a, b)

$$C_i = f_{i,d} [(C_{i,\text{sat}} - C_{j,\text{sat}}) f_{i,d} + C_{j,\text{sat}}] \quad (9-12)$$

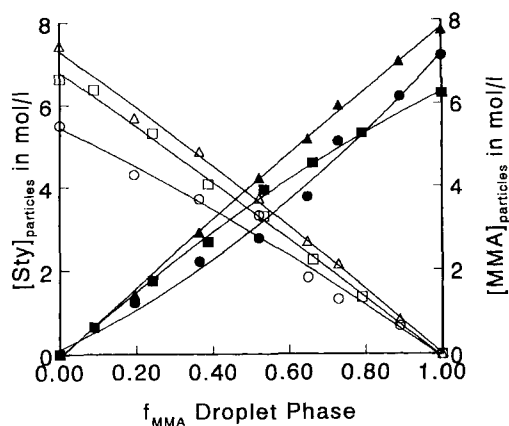
A similar expression can be deduced for monomer  $j$ . Figures 9-2 and 9-3 represent the partitioning of styrene and methyl methacrylate between monomer droplets and polymer particles consisting of poly(styrene-*co*-methyl methacrylate) and polybutadiene-*graft*-poly(styrene-*co*-methyl methacrylate), respectively (Aerdts et al., 1993). As shown in Figs. 9-2 and 9-3, the experimental data can be described by the developed model, i.e., by Eq. (9-12). Figure 9-4 displays the mole fraction of methyl methacrylate in the polymer particles as a function of the mole fraction of methyl methacrylate in the monomer droplets with  $\chi=0.2$  and  $\gamma=45$  mN/m (this is the surface tension between the surfactant and water). Here again, the experimental results can be described by the developed model extremely well.

The above-discussed thermodynamic model for describing, explaining, and predicting monomer partitioning during an emulsion polymerization has also been successfully applied to the swelling of phospholipid bilayers by an organic solvent (Maxwell and Kurja, 1995).

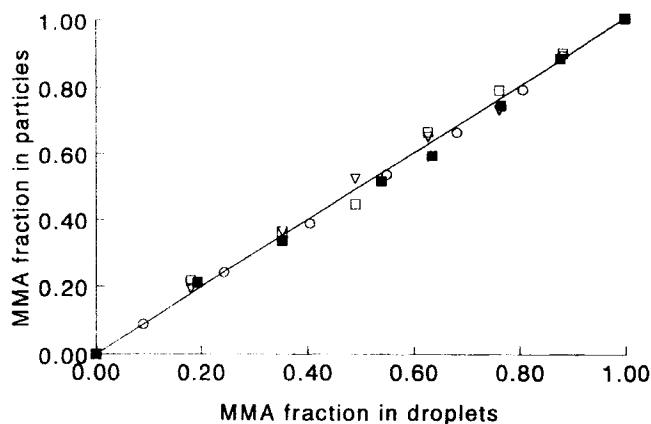
In conclusion, it can be said that the partitioning behavior of monomers between the different phases present during an emulsion polymerization can be described and predicted using a simple thermodynamic model derived from the classical Flory-Huggins theory for polymer solutions.



**Figure 9-2.** Experimentally determined monomer concentrations in the polymer particles as a function of the fraction of methyl methacrylate in the droplet phase (symbols) compared with theoretical predictions according to Eq. (9-12) (full lines), where  $[MMA]_{\text{sat}}=7.00$  mol/l and  $[S]_{\text{sat}}=5.56$  mol/l; Methyl methacrylate concentrations (open circles) and styrene concentrations (closed squares) in poly(styrene-*co*-methyl methacrylate) (25/75).



**Figure 9-3.** Experimentally determined monomer concentrations in the polymer particles as a function of the fraction of MMA in the droplets (symbols) compared with the theoretical predictions of Eq. (9-12) (lines): Styrene concentrations in SMMA-free (open circles) ( $[S]_{\text{sat}}=5.51$  mol/l), SMMA-*graft* (open triangles) ( $[S]_{\text{sat}}=7.44$  mol/l), and PB (open squares) ( $[S]_{\text{sat}}=6.64$  mol/l); MMA concentrations in SMMA-free (closed circles) ( $[MMA]_{\text{sat}}=7.16$  mol/l), SMMA-*graft* (closed triangles) ( $[MMA]_{\text{sat}}=7.77$  mol/l), and PB (closed squares) ( $[MMA]_{\text{sat}}=6.25$  mol/l) in a polybutadiene-*graft*-poly(styrene-*co*-methyl methacrylate).



**Figure 9-4.** Experimentally determined fractions of methyl methacrylate (MMA) in the droplet phase as a function of the fraction of methyl methacrylate in different polymer particles: MMA and styrene in PB (open circles), SMMA-free (open squares), and SMMA-graft (open triangles) from polybutadiene-graft-poly(styrene-co-methyl methacrylate) polymer particles, while the closed squares represent a poly(styrene-co-methyl methacrylate) latex swollen with styrene and MMA. The solid line gives the theoretical prediction according to Eq. (9-11).

### 9.3.3 Composition Drift in Emulsion Co- and Terpolymerization

A special aspect of (emulsion) copolymerization is the occurrence of composition drift. In combination with the instantaneous heterogeneity (statistical broadening around the average chemical composition), this phenomenon is responsible for the chemical heterogeneity of the copolymers formed. Composition drift is a consequence of the difference between instantaneous copolymer composition and overall monomer feed composition. This difference is determined by: (a) the reactivity ratios of the monomers (kinetics) and (b) the monomer ratio in the main loci of polymerization (i.e., the polymer particles), which can differ from the overall monomer ratio of the feed (as added according to the recipe), which in turn is caused by monomer partitioning. In most cases the monomer ratio in the polymer particles equals the monomer ratio in the monomer droplets; the water solubility of the monomers is therefore the main factor that has an effect on the monomer ratio in the polymer particles. A list of water solubilities of some common monomers is given in Appendix II.

In principle, on comparing solution or bulk copolymerization to emulsion copol-

ymization, two situations can be distinguished: (1) If the more reactive comonomer is the less water soluble one, then there will be a stronger composition drift as the amount of water increases in the recipe [e.g., styrene-methyl acrylate (Schoonbrood et al., 1995a)]; (2) If the more reactive comonomer is the more water soluble one, then a smaller composition drift can occur as the amount of water increases [e.g., indene-methyl acrylate, methyl acrylate-vinyl 2,2-dimethyl-propanoate (Noel et al., 1994)]. In the latter cases the composition drift may even be reserved at very high water contents.

In order to be able to describe and control an emulsion copolymerization, both the reactivity ratios and monomer partitioning (Sec. 9.3.2) have to be known.

There are three experimental data sets (exp. data as a function of feed composition) that can be used to obtain information on the copolymerization model to be used (Sec. 9.3.1) and on the reactivity ratios:

- Chemical composition: This is in general properly described by the ultimate model.
- Triad fractions: These are determined by the same conditional probabilities as the composition.

- Propagation rate constants ( $k_p$ ): the penultimate model is favored here in most cases.

In general it is found that the chemical composition (distribution) can be described by the ultimate model and  $k_p$  by the implicit penultimate model. Although this situation seems surprising at first sight, it is possible when  $r_{21}=r_{11}$  and  $r_{12}=r_{22}$ .

In this restricted penultimate model there are four reactivity ratios ( $r_1, r_2, s_1, s_2$ ); the  $r$ -values are usually determined from compositional data and the  $s$ -values can then be determined by fitting these to the  $k_p$  data (see also Sec. 9.3.1).

Batch processes are known to give two-peaked distributions of copolymer composition when a strong composition drift occurs during the course of the (emulsion) copolymerization. Moreover, in emulsion copolymerization the degree of bimodality appears to depend on the monomer/water ratio (Guillot, 1987; Van Doremaele, 1990; Schoonbrood et al. 1995a). Semi-continuous processes (i.e., addition of monomer during polymerization) can be used to prepare more homogeneous copolymers. Dynamic mechanical spectroscopy or differential scanning calorimetry and transmission electron microscopy combined with preferential staining techniques have been used to determine the possible occurrence of phase separation due to double-peaked chemical composition distributions (CCDs). It has been shown that the compositional heterogeneity of the copolymer has a dramatic effect on the mechanical properties (Schoonbrood et al., 1995a).

### 9.3.3.1 Ternary Emulsion Copolymerization

In the fundamental investigations described in the literature dealing with emul-

sion copolymerization, most attention has been given to binary copolymerization, i.e., the polymerization of two monomers. Far less attention has been paid to ternary emulsion copolymerization (three monomers), hereafter referred to as terpolymerization. Emulsion terpolymerization investigations, mostly dealing with properties and applications, have been published mainly as patents.

It is obvious that the typical aspects that distinguish emulsion copolymerization from homopolymerization, e.g., monomer partitioning, the dependence of kinetics on the local monomer concentration ratio, etc., are rapidly becoming more complex when three monomers are involved, not to mention the complications in terpolymer analysis.

However, since it can easily be understood that using three monomers gives the possibility to obtain an even larger variety and refinement of copolymer properties, more effort is being put into research on emulsion terpolymerization, although it is to be expected that there will be little or no fundamental, mechanistic differences between binary and ternary emulsion copolymerization systems.

So far the majority of papers that have appeared in the literature about terpolymerization only relate the average terpolymer composition to the terpolymer properties (Coker, 1975; Saric and Janovic, 1983, Wallace and Chen, 1985). The microstructure of emulsion terpolymers of vinyl chloride, vinylidene chloride, and hydroxyethyl acrylate, prepared in batch and semi-continuous reactions, were studied by means of differential scanning calorimetry (DSC) and  $^{13}\text{C}$  NMR (nuclear magnetic resonance) (Pou-rahmady and Bak, 1990). Schoonbrood studied the emulsion terpolymerization of styrene, methyl methacrylate, and methyl acrylate (Schoonbrood, 1996), and for the



first time he also determined the propagation rate coefficients for this ternary system by means of pulsed laser polymerization (Schoonbrood et al., 1995b). He also determined and predicted the microstructure (in terms of CCD) of these terpolymers (Schoonbrood et al., 1996).

In many cases two relatively water-insoluble comonomers (e.g., styrene, butyl acrylate, methyl methacrylate) are used and small amounts of a third, highly water-soluble comonomer (Ronel and Kohn, 1975; Huo et al., 1988; Bonardi et al., 1989) [e.g., (meth)acrylic acid, 2-hydroxyethyl methacrylate] or even a surface-active comonomer (Guillaume et al., 1990). These water-soluble comonomers are generally introduced to obtain functionalized latices, for example, to improve the adhesive product properties or to prepare reactive latices (see Sec. 9.5.1).

### 9.3.4 Chemical Composition

#### Distribution and Molar Mass Chemical Composition Distribution

The molecular microstructure can be characterized in terms of sequence distribution, tacticity, molar mass distribution (MMD, see Sec. 9.2.4), and chemical composition distribution (CCD). These can be combined in a three-dimensional distribution of molar mass and chemical composition (MMCCD). In addition to the intramolecular sequence distribution, the molecular microstructure not only comprises the averages of molar mass and chemical composition but also their complete distributions as a whole (MMCCD). The MMCCD can be considered as a fingerprint of all the molecular events that contribute to polymer growth, and it constitutes the linkage between the fundamental mechanistic chemical processes occurring in the reaction loci (Stockmayer, 1945; Koenig, 1980) and the

copolymer properties (Rodriquez, 1983). Therefore it is generally recognized that a detailed revelation of the copolymer microstructure is a major factor contributing to a better understanding of both the process and the polymer properties, and that, in the detailed modeling of the entire emulsion copolymerization process, microstructural modeling is a prerequisite.

Several experimental techniques have now become available to determine not only the average copolymer composition but also the complete MMCCD (Tacx and German, 1989b; Glöckner, 1989). In general, two chromatographic separation techniques are combined in the determination of the MMCCD, one based on the separation according to molar mass, where the exclusion mechanism is operable, and the other based on separation according to chemical composition, where solubility and column adsorption contribute to the separation mechanism. Together with experimental sequence distribution information obtained by means of NMR, detailed information about the copolymer microstructure was gained by Van Doremale (1990), while also providing the necessary experimental proof of the reliability of the model calculations.

A limited number of models for calculating the (instantaneous) (MM)CCD and the sequence distribution of emulsion copolymers has been developed in the last few years, using either kinetic (i.e., stochastic) (Storti et al., 1990; Van Doremale et al., 1990) or probabilistic approaches (Giannetti et al., 1988b).

German and co-workers developed methods of experimentally measuring the (MM)CCDs of emulsion copolymers of styrene-ethyl methacrylate, but in the first instance did not make the comparison with applicable model calculations (Tacx and German, 1989a, b). The copolymers were separated according to molar mass by means of

size exclusion chromatography (SEC) and each SEC fraction was subsequently analyzed according to chemical composition by means of either gradient elution quantitative thin layer chromatography (TLC/FID) or gradient high performance liquid chromatography (HPLC). In both cases, a gradient of a solvent and nonsolvent is applied to the copolymer. Later they also developed the MMCCD determination of emulsion styrene–methyl acrylate copolymers (Van Doremaele et al., 1991) and compared the results with appropriate model calculations. Guillot and co-workers (Ramirez-Marquez, 1987; Ramirez-Marquez and Guillot, 1988) investigated several styrene–acrylate (S–MA) emulsion copolymers using differential scanning calorimetry (DSC) in an attempt to determine the copolymer CCD. Unfortunately, this technique does not give the full MMCCD, but only (fractional) average compositions.

Guillot and co-workers reported aqueous phase polymerization in the case of S–MA (Ramirez-Marquez and Guillot, 1988), vinyl acetate–butyl acrylate (VAc–BA) (Kong et al., 1988), and styrene–ethyl acrylate (S–EA) (Djekhaba et al., 1988) batch emulsion copolymerization. Capek et al. (1985) reported similar behavior for acrylonitrile–butyl acrylate. Polymerization in the aqueous phase results in the formation of copolymer that is enriched in the water-soluble monomer. This effect is enhanced by low monomer/water ratios. This effect is expected to show up most explicitly during interval I (the nucleation stage). During intervals II and III, the (co-)oligomers formed in the aqueous phase were shown to be scavenged by the polymer particles at already relatively short length. Neglecting aqueous phase polymerization, which generally comprises less than 1% of the total amount of polymer formed (Arzamendi and Asua, 1990), the monomer ratio inside the

polymer particles, together with the reactivity ratios, mainly governs the instantaneous copolymer composition.

### 9.3.5 Process Strategies in Emulsion Copolymerization

The emulsion polymerization strategy, i.e., the kind of process, can have considerable effect on the molecular structure and particle morphology. The intrinsic factors as well as the process conditions determine the colloidal aspects of the copolymer latex (particle diameter, surface charge density, colloidal stability, etc.), the characteristics of the polymeric material in the particles (MMCCD, see Sec. 9.3.4), and the structure of the particles (copolymer composition as a function of particle radius, etc.). In turn, these factors determine the properties of the latex and the copolymer product.

The ultimate goal of most of the investigations on emulsion copolymerization is to be able to control the process in such a way as to produce a copolymer product (latex or coagulate) with the desired properties. For this purpose the semi-continuous (sometimes called semi-batch) emulsion copolymerization process is widely used in industry. The main advantages of this process as compared with conventional emulsion batch processes include convenient control of the emulsion polymerization rate in relation to heat removal and control of the chemical composition of the copolymer and the particle morphology. These are important features in the preparation of speciality or high performance polymer latices.

Semi-continuous emulsion copolymerization processes can be performed by applying various monomer addition strategies:

### 9.3.5.1 Constant Addition Strategy

The most widely investigated and described procedure is the addition of a given mixture of the monomers (sometimes pre-emulsified monomers) at a constant rate (Šnupárek, 1985; Rios et al., 1985; Omi et al., 1985).

For instance, this procedure is followed in many papers dealing with the semi-continuous emulsion copolymerization of vinyl acetate and butyl acrylate (e.g., El-Aasser et al., 1983). With respect to the monomer addition rate, two main situations can be distinguished: (a) Flooded conditions: The addition rate is higher than the polymerization rate. (b) Starved conditions: The monomers are added at a rate lower than the maximum-attainable polymerization rate (if more monomer were present). The latter process (starved conditions) is often applied in the preparation of homogeneous copolymers/polymer particles. In this case, after some reaction time, a steady state is attained because of the low addition rates in which the polymerization rate of each monomer is equal to its addition rate. A copolymer is made with a chemical composition identical to that of the monomer feed. Sometimes semi-continuous processes with a variable feed rate (power feed) are used to obtain polymer particles with a core-shell morphology (Basset, 1983).

### 9.3.5.2 Controlled Composition Reactors

Intelligent monomer addition strategies in copolymerizations strongly rely on the monitoring of monomer conversions. In copolymerization, control of the copolymer composition can also be obtained when applying monomer addition profiles. These monomer addition profiles can either be based on the direct translation of on-line

measurements to monomer addition steps (controlled composition reactor), or the profiles can be predicted by emulsion copolymerization models on a conversion basis. The required conversion–time relation is then obtained by on-line measurements. The process of filtering the obtained conversion data with the aid of a polymerization model, the so-called Kalman-filtering (Chien and Penlidis, 1990) or the model reference adaptive control (Leiza et al., 1992–93), makes it possible to accurately control the process and to obtain the desired microstructure. On-line methods of determining monomer conversion are, as outlined above, important for controlling the emulsion (co)polymerization process. Excellent reviews have appeared on on-line sensors for polymerization reactors (Chien and Penlidis, 1990; Schork, 1990; German et al., 1997).

### 9.3.5.3 Optimal Addition Profile

Arzamendi and Asua (1989) developed the so-called optimal monomer addition strategy. By using this method, Arzamendi and Asua demonstrated that within a relatively short period of time homogeneous vinyl acetate (VAc)–methyl acrylate (MA) emulsion copolymers can be prepared in spite of the large difference between the pertaining reactivity ratios. The reactor was initially charged with all of the less reactive monomer (i.e., VAc) plus the amount of the more reactive monomer (i.e., MA) needed to initially form a copolymer of the desired composition. Subsequently, the more reactive monomer (MA) was added at a computed (time variable) flow rate (optimal addition profile) in such a way as to ensure the formation of a homogeneous copolymer.

The key problem in this method is the calculation of the amount of methyl acrylate to be initially charged in the reactor and the op-

timal addition rate profile of the remaining amount of methyl acrylate. The calculations are based on the following assumptions:

- a) Copolymerization is carried out starting from a monodisperse seed latex of the desired composition.
- b) The number of particles remains constant during the reaction.
- c) Aqueous phase polymerization is negligible.
- d) Thermodynamic equilibrium determines the various monomer concentrations.

By applying the instantaneous copolymer composition equation, the desired monomer concentration ratio inside the polymer particles is calculated. In combination with the thermodynamic equilibria equations, this ratio allows the calculation of the amount of methyl acrylate to be initially charged in the reactor.

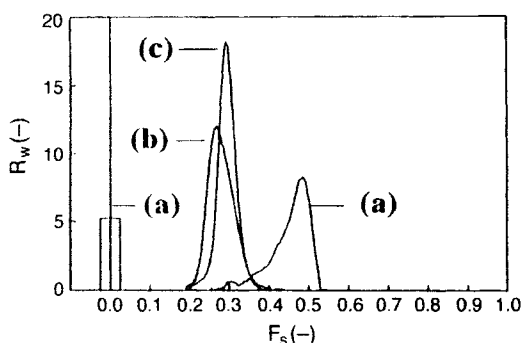
Arzamendi and Asua (1989) applied a semi-empirical method to calculate the time-dependent evolution of  $\bar{n}$ . This evolution is calculated from a semi-continuous experiment carried out under similar conditions as the final optimal process, but applying an estimated, constant addition rate of methyl acrylate. The evolution of  $\bar{n}$  is correlated with the volume fraction ( $f_p$ ) of polymer in the particles. This correlation is then used to calculate an addition profile. Another semi-continuous experiment is then carried out using this addition profile. If the copolymer composition deviates too much from the desired value, another correlation of  $\bar{n}$  with  $f_p$  is then calculated from the last experiment. This procedure can be repeated until the addition profile is optimal.

Alternatively, Van Doremaele (1990) applied an even more pragmatic approach. This method can be applied without actually calculating  $\bar{n}(t)$  or  $\bar{n}(f_p)$  and may therefore be more generally applicable. This method was applied to the emulsion copoly-

merization of styrene (S) and methyl acrylate (MA). The batch emulsion copolymerization of S and MA is known to often produce highly heterogeneous copolymers (styrene being the more reactive and less water-soluble monomer).

Rather than a large difference between the reactivity ratios (VAc-MA), the large difference between the water solubilities of S and MA is the main problem here. As stated, the time-evolution of  $\bar{n}$  was not actually calculated but it was set equal to 0.5 as a first estimation. It would be highly fortuitous if the first estimated addition profile, based on  $\bar{n}=0.5$ , was optimal, because the average number of radicals will generally deviate from this first estimation (i.e.,  $\bar{n}=0.5$ ). Nevertheless, a first addition profile was calculated, presuming  $\bar{n}=0.5$ . Separately, the correlation between the amount of styrene to be added and the conversion was calculated from thermodynamic equilibrium data which would lead to the desired copolymer composition. Combining the results, i.e., the conversion-time curve from the experiment carried out with this addition profile and the correlation between the amount of styrene to be added and conversion, a new addition profile could be calculated. In the case of the S-MA system the iteration converges rapidly; only four iteration steps appeared to be required in S-MA emulsion copolymerization to arrive at indistinguishable monomer addition rate profiles.

In order to evaluate the results, Van Doremaele analyzed the copolymers formed by means of high performance liquid chromatography (HPLC), providing detailed microstructural information (i.e., chemical composition distribution, CCD) of the copolymers. In Fig. 9-5 the CCDs are depicted of three high conversion S/MA copolymers having the same average chemical composition but prepared by different process-



**Figure 9-5.** CCDs, experimentally determined with HPLC, of three styrene/methyl acrylate emulsion copolymers, all with  $F_s=0.25$  and  $(M/W)_0=0.2$  (g/g): (a) semi-continuous, starved conditions (32 h), (b) semi-continuous, optimal addition profile (5 h), (c) conventional batch process (3 h). [Reproduced with permission from Van Doremale (1990).]

es. The one prepared by the conventional batch process exhibits bimodality, has two glass transition temperatures, and has a minimum film formation temperature of 17°C. Both the one prepared in a semi-batch process under starved conditions (32 h) and the one obtained in a semi-continuous process while applying the optimal monomer addition strategy (5 h) are homogeneous with respect to chemical composition and have a minimum film formation temperature of 27°C. In general it can be stated that the reactions based on the optimal addition rate profile proceed more rapidly than those based on constant addition rate strategies.

### 9.3.6 Batch, Semi-Batch, and Continuous Emulsion Polymerization

Commercial emulsion polymerizations are usually carried out in batch or semi-batch reactors. Almost complete conversion can be obtained and the preparation of different products is possible in the same reactor.

For the production of large amounts of the same product, the use of a continuously op-

erated stirred tank reactor (CSTR) would be preferable because of its lower operating costs and its more consistent product quality. For copolymerization, in a single CSTR a completely homogeneous copolymerization can be produced (Van den Boomen et al., 1996). The disadvantage of polymerization in a single CSTR arises from the residence time distribution, which leads to products with a much lower conversion, a lower particle concentration, and a much broader particle size distribution when compared to batch (Nomura et al., 1971; DeGraff and Poehlein, 1971).

Further sustained oscillations in conversion and particle concentration occur for a lot of recipes (Kiparissides et al., 1980). This can be overcome, in principle, by the development of a continuous reactor system where the stage of particle nucleation is spatially separated from the other stages of the process. A small plug flow reactor as a seed reactor followed by a CSTR, or a pulsed packed column (PPC), are examples for continuous emulsion polymerization (Hoedemakers and Thoenes, 1990). In the PPC, good local agitation is combined with lower flow rates and little backmixing, which provides the same conversion and particle concentration as the equivalent batch process (Hoedemakers and Thoenes, 1990; Meuldijk et al., 1992). Proper control of the intermolecular composition distribution seems to be possible with a series of CSTRs (Van den Boomen 1997).

## 9.4 Particle Morphologies

### 9.4.1 Introduction to Particle Morphologies

Composite polymer particles are usually prepared by seeded emulsion polymerization. In the first stage, well-defined particles are prepared, while in the second stage an-

other monomer is polymerized in the presence of these well-defined particles. Multi-stage emulsion polymerization produces structures such as core-shell (Min et al., 1983; Hourston et al., 1986), "inverted" core-shell (Muroi et al., 1984; Lee and Ishikawa, 1983), and phase-separated structures such as sandwich structures (Cho and Lee, 1985), hemispheres (Cho and Lee, 1985; Stutman et al., 1985), "raspberry-like" (Okubo et al., 1980a, b), and void particles (Okubo et al., 1981, 1982). Control of the composite polymer particle morphology is important for many latex applications, such as adhesives and coatings (Vandezande and Rudin, 1994), and the impact modification and toughening of polymer matrices (Lovell, 1995). The structures have a major influence on the properties. The particle morphology can be affected by many of the polymerization parameters and conditions, for examples, water solubility of the monomers; type, amount, and addition mode of other ingredients such as surfactant, initiator, chain transfer, or crosslinking agents, degree of compatibility of the polymers, viscosity of the polymerization loci (swelling of the core particle and the molar mass of polymer), degree of grafting of the second stage polymer onto the core particle, polarity of the polymers, interfacial tension at the polymer-polymer and polymer-water interphases, degree of crosslinking, methods of monomer addition, and polymerization temperature.

Modeling the particle morphology is extremely complex and no broadly applicable approach is available yet. Particle morphology can be controlled by kinetics and/or thermodynamics. A thermodynamic approach is described where the interfacial tensions between the two polymers and between each of the polymers and water are the determining factors. Calculations of the polymer particle morphology on the basis of

minimization of the interfacial energy change have been reported by Sundberg et al. (1990) and Chen et al. (1991a, b). The morphology may also be determined by kinetic processes, as described by Chern and Poehlein, (1987, 1990a, b) and Mills et al., (1990). The interfacial tension seems to be one of the main parameters controlling particle morphology in composite latexes. Depending on the type of initiator, the surface polarity can be different, and therefore also the particle surface polarity rather than the polymer bulk hydrophilicity could be the controlling parameter in determining which phase will be inside or outside in composite particles. The kinetic parameters (such as the viscosity at the polymerization loci, molar mass of the polymers, and mode of addition of the second stage monomer) influence the rate of formation of a certain morphology which is basically determined by the interfacial tensions (Chen, 1993). Asua and González-Ortiz (González-Ortiz and Asua, 1996a, b) also developed a mathematical model for the development of particle morphology in emulsion polymerization. This model is based on the migration of clusters. The clusters are formed if the newly formed polymer chain is incompatible with the polymer existing at the site where it is formed, thus inducing phase separation. The equilibrium morphology is reached when the polymer chains diffuse into the clusters and the clusters migrate in order to minimize the Gibbs free energy. This motion of the clusters is due to the balance between the van der Waals forces and the viscous forces.

Particle morphologies with more than three phases have been studied by Sundberg and Sundberg (1993). Characterization of the particle morphologies is very important in order to control the seeded emulsion polymerizations and to achieve certain properties. The different applications of the core/

shell particles require advanced characterization techniques to determine the morphology down to the molecular level. Important and powerful characterization techniques are, for example, transmission electron microscopy (TEM) (Lee and Rudin, 1992), scanning electron microscopy (SEM), small angle neutron scattering (Hergeth et al., 1989), light scattering (Mills et al., 1993, Ottewil et al., 1995), and NMR (Clauss et al., 1993). Moreover, it is also important to know whether the composite polymer particles contain graft or block copolymers, since these may act as compatibilizers and thus have a large effect on the extent of phase separation. For these detailed characterizations, chromatographic techniques, titrations, and extraction methods are very useful.

#### 9.4.2 Core–Shell Morphologies

It is not obvious if seeded emulsion polymerization always leads to core/shell morphologies. This has been discussed in Sec. 9.4.1. The design of the core/shell particles is dictated by the desired properties and applications. The properties that core/shell polymer particles exhibit depend on a number of parameters, such as the polymer or copolymer type, the molar mass, the amount of grafted material between the core and the shell, the particle size and particle size distribution, the relative proportion of the core to the shell material, and the  $T_g$  of the polymer in the core and in the shell. Three main types of core/shell composite particles can be distinguished, i.e., composite particles with organic or inorganic cores, and those with an ‘empty’ core, the so-called hollow particles. These three types will be discussed in the following sections.

##### 9.4.2.1 Organic Cores

The cores of organic composite polymer particles can be varied along with the desired properties. The most important parameters of the polymer in the core are the glass transition temperature ( $T_g$ ), the molar mass, the crosslink density, and the type of (co)polymer. Composite polymer particles used for impact modification consist of a rubbery core and a glassy shell which is miscible or can react with the matrix. Examples of such types of polymer are the very important acrylonitrile–butadiene–styrene (ABS) composite polymer and also the methyl methacrylate–butadiene–styrene transparent composite polymer for the impact modification of PVC. The latter example has been modified with glycidyl methacrylate in order to perform reactive extrusion with a polyamide (Aerdt et al., 1997). For coating applications, the polymer particles often consist of a glassy core and a low  $T_g$  shell which facilitates the film-forming properties (Vandezande and Rudin, 1994).

##### 9.4.2.2 Encapsulation of Inorganic Particles

###### *Applications of Micro-encapsulated Particles*

The micro-encapsulation of pigment and filler particles is an important area of research, both in the academic research world and in industrial laboratories. Much activity in the past decade has been aimed at obtaining inorganic powders coated with an organic polymer layer. Such systems are expected to exhibit properties other than the sum of the properties of the individual components. In general, several benefits from this encapsulation step can be expected when the particles are incorporated in a polymeric matrix (e.g., plastics or emulsion paints):

- Better particle dispersion in the polymeric matrix.
- Improved mechanical properties.
- Improved effectiveness at light scattering in a paint film.
- Protection of the filler or pigment from outside influences.
- Protection of the matrix polymer from interaction with the pigment.
- Improved barrier properties of a paint film.

The applications of these encapsulated particles relate to the above-mentioned benefits and the particles can be found in filled plastics, paints, inks, paper coatings, etc. (Hofman-Caris, 1994; Van Herk and German, 1997).

A very important application of encapsulated pigment and filler particles is in emulsion paints. One of the more expensive components of waterborne paints is the white pigment, usually titanium dioxide (rutile form). The pigment is added to obtain hiding power. The hiding power or opacity depends on the occurrence of light absorption and light scattering. For pigments with a high refractive index, like titanium dioxide, light scattering forms the main contribution to the hiding power. The light-scattering effectiveness of the pigment particles depends on their particle size and on the interparticle distance. Agglomerates of pigment, already present in the wet paint film or formed by flocculation during the drying process, will reduce the scattering effectiveness of the dispersed pigment particles. By encapsulating the pigment particles, it is expected that the chance of flocculation is reduced and that the dispersion in the final paint film is improved. It has been suggested that the layer thickness could be optimized to obtain optimum spacing between the titanium dioxide particles to achieve maximum light scattering (Templeton-Knight, 1990).

In encapsulating the pigment particle an important adverse effect of the pigment could be influenced, that is, the generation of radicals under the influence of UV light. These radicals can lead to degradation of the matrix polymer and thus lead to reduced durability. With proper choice of the polymer layer, the durability might also be improved. Other advantages are improved block resistance, less dirt pick up, better adhesion (Hoy and Smith, 1991), and improved chemical resistance (Godard et al., 1989).

For the above-mentioned reasons, most commercial pigments already have inorganic and/or organic surface modifications. An additional benefit can be brought about by the formation of multi layers of polymer on inorganic particles (Janssen et al., 1993a), where additional, for example, rubber toughening effects can be introduced (Kolarik et al., 1990). Other applications of encapsulated pigments can be found in inks, paper coatings, and electro-photographic toners.

When the inorganic particles are magnetically responsive, pathways open to special applications like the coupling of enzymes and antibodies to the surface of the magnetic particles, after which drug targeting becomes possible. These particles can also be used in biochemical separations (Arshady, 1993). Furthermore, magnetic particles can be used in magnetic recording media, oil spill clean up, and moldable magnetic powders (Buske and Goetze, 1983). Huang (1986) described the preparation of magnetic polymer particles through inverse emulsion polymerization. He encapsulated iron oxide with crosslinked hydrophilic polymer. These particles can be used as a seed to prepare aqueous hydrophobic magnetic polymer particles. The use of encapsulated particles as catalyst carriers has recently been reported (Hong and Ruckenstein, 1993).



### Principle of Encapsulation Through Emulsion Polymerization

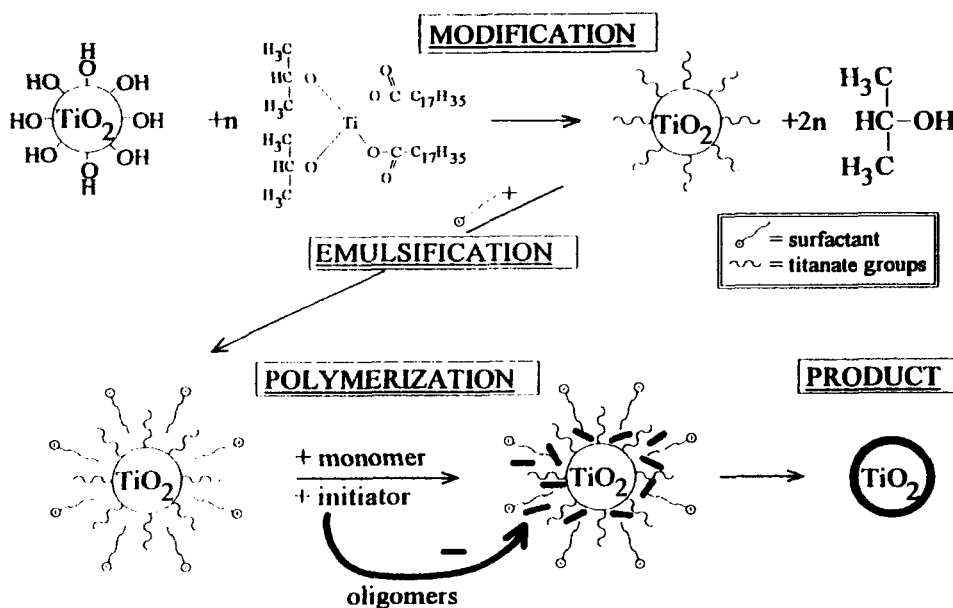
The inorganic particles (after hydrophobization) are dispersed with the normal surfactants and an emulsion polymerization is performed where the locus of polymerization is the hemi- or admicelle around the inorganic particle (Janssen et al., 1993b) (Fig. 9-6).

Usually 'maximum' properties are obtained when the inorganic particles are distributed evenly and as single (primary) particles in the matrix. This means that, in the steps towards obtaining the final product, keeping the particles well dispersed is of major importance. Initially the particles should be well dispersed in the aqueous phase and (partial) coagulation during the emulsion polymerization must be avoided, because this leads to irreversible fixation of the coagulates.

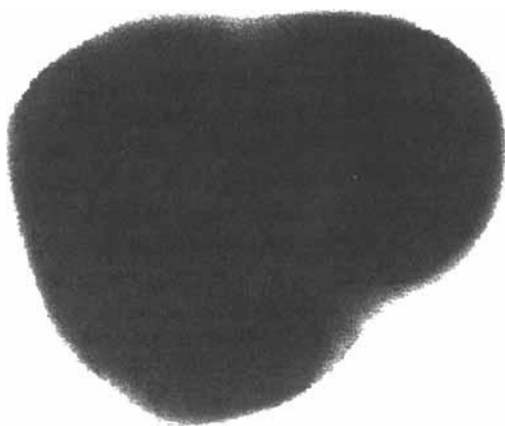
In order to be able to disperse the inorganic particles in an aqueous medium, spe-

cial stabilizing agents for the inorganic particles should be added, or the surface should be hydrophobized in order to be able to use conventional emulsion polymerization surfactants. Ultrasound has been applied to improve the dispersion of the pigment particles (Templeton-Knight, 1990; Lorimer et al., 1991). Many types of pigment particle can be obtained commercially with organic surface modifications, or alternatively they can be modified with silanes or titanates. Polymerization on the surface is in competition with the process of new, pure polymer particle formation. Therefore the normal stabilization with micelle-forming surfactants is not straightforwardly applicable, and the surface area offered by the inorganic particles is very important (Janssen, 1995) (Fig. 9-7).

Using less water soluble monomers in combination with a nonionic initiator, the formation of surface active oligomers in the aqueous phase can be minimized, thus increasing the encapsulation efficiency. Jans-



**Figure 9-6.** Schematic representation of encapsulation of inorganic (submicrometer) particles through emulsion polymerization.



**Figure 9-7.** Transmission electron micrograph of the product of an encapsulation of  $\text{TiO}_2$  with polymethyl methacrylate (Janssen, 1995) showing an encapsulated particle.

sen (1995) used cumene hydroperoxide in combination with iron (II) sulfate as a reductor, thus aiming at initiation at the hydrophobic/hydrophilic interface of the modified  $\text{TiO}_2$  particles.

In order to improve compatibility between the polymer layer and the matrix, it is interesting to vary the composition of the polymer layer by copolymerization. In this way the glass transition temperature ( $T_g$ ) of that layer can also be adjusted. Several copolymerizations were performed on titanium dioxide pigment particles, including the monomer combinations styrene (S)/methyl acrylate (MA), styrene/methyl methacrylate (MMA), and methyl methacrylate/butyl methacrylate (BMA) (Janssen et al., 1993a; Van Herk et al., 1993). On increasing the MA content in the S/MA copolymerizations (Table 9-4), the encapsulation efficiency decreases.

On increasing the water solubility of the monomer in a homopolymerization or increasing the content of this water-soluble comonomer in a copolymerization, the efficiency decreases (Table 9-4).

**Table 9-4.** Efficiency and glass transition temperatures<sup>a</sup>.

Monomers	Ratio	Efficiency <sup>b</sup>	Polymer content <sup>c</sup>	$T_g$ (°C)
		(mol/mol) (wt.%)	(wt.%)	
MMA	—	7.0	5.7	
MMA/BMA	1.390	8.6	11.6	
S/MMA	0.920	8.6	6.9	
S	—	33.4	25.0	103.6 <sup>d</sup>
MA	—	6.6	6.2	5.7
S/MA	0.082	4.8	8.7	17/65
S/MA	0.827	6.8	11.7	50.0
S/MA	1.000	7.7	12.6	65.0 <sup>e</sup>
S/MA	1.654	7.8	12.8	75.0

<sup>a</sup> Data from Janssen et al. (1993a) and Van Herk et al. (1993); <sup>b</sup> efficiency: weight percentage of monomer reacted to the surface; <sup>c</sup> polymer content: weight percentage polymer of the encapsulated particles; <sup>d</sup> free polymer shows a  $T_g$  of 99°C; <sup>e</sup> free polymer shows two  $T_g$ s of 7 and 67°C.

In conclusion, it can be said that the smaller the inorganic particles, the more efficient encapsulation reactions proceed. To encapsulate particles larger than 500 nm, other approaches than emulsion polymerization should be applied, for example, heterocoagulation with in situ formed (unstable) polymer particles (Van Herk and German, 1998).

A new approach is the use of special surfactants that can form bilayers on the surface of inorganic particles. These twin-tailed surfactants are normally used to prepare vesicles (Van Herk and German, 1998) (see also Sec. 9.4.2.3).

#### 9.4.2.3 Hollow Particles

The preparation of hollow particles through emulsion polymerization is very interesting, for instance, in the light of using these particles as drug carriers in controlled drug release (Juliano and Layton, 1980). Other applications are in surface coatings and as opacifiers.

In principle, there are two routes to obtain hollow particles through emulsion polymerization; one possibility is preparing particles that after isolation undergo a further treatment to render them hollow, the other route is designing the synthesis in such a manner that hollow particles are obtained directly. The first route starts with the preparation of core-shell particles. The core can then either be removed by dissolving it in an appropriate solvent, or it could shrink more strongly than the shell upon drying or treatment with an acid or a base. The second route can be based on various vesicle polymerizations strategies.

#### *Core-Shell Emulsion Polymerization*

Vanderhoff et al. (1991) prepared particles consisting of a core of a copolymer of methacrylic acid and methyl methacrylate and a shell of crosslinked material. After neutralization with  $\text{NH}_4\text{OH}$ , the core material dissolves and the particles contain voids of between 130 and 760 nm. A similar approach was applied by Okubo and Ichikawa (1994), where the particles were produced by an emulsion-free terpolymerization of styrene, butyl acrylate, and methacrylic acid. The effects of pH, temperature, and time of acid treatment on the multi hollow structure formed were investigated.

A somewhat different approach is where an organic solvent is used to extract the core material. In one example (Okubo et al., 1991; Okubo and Nakagawa, 1994), large polystyrene seed particles, produced by dispersion polymerization, were used as a seed in a second stage polymerization where a shell of polystyrene-divinylbenzene was polymerized around the core. The core material was then extracted with toluene under reflux. Depending on the divinylbenzene content, particles could be obtained with

structures ranging from one void to a fine multi-voided structure.

#### *Vesicle Polymerization*

There are several ways to achieve polymerization in or of vesicles (Paleos, 1990):

- 1) Polymerize the surfactant molecules when these contain polymerizable groups.
- 2) Polymerize the counterions of the surfactants.
- 3) Polymerize monomer that is contained in the bilayer.
- 4) A combination of 1 or 2 and 3.

The most flexible route is the one where the bilayer is swollen with the monomers of choice. In this case the glass transition temperature, permeability, layer thickness, and degradability of the polymer layer can be varied more easily than in the other approaches.

One of the first reports on polymerizing monomer in vesicle bilayers stems from Kurja et al. (1993). Recently Poulain et al. (1996) described the polymerization of isodecyl acrylate in vesicles made of sodium di-2-ethylhexyl phosphate. The polymerization was either initiated by potassium persulfate or azo-bis-isobutyronitrile. Hollow particles with a mean diameter of 50 nm were obtained. An extensive overview of vesicle polymerization is given by Kurja et al. (1996). A report on the use of adsorbed bilayers to encapsulate inorganic particles, using surfactants that normally form vesicles, will appear soon (Zirkzee, 1997). A critical step in vesicle polymerization is swelling the preformed vesicles with monomer. Care must be taken that the vesicles do not break up during this step (Kurja et al., 1993; Poulain et al., 1996).

## 9.5 Special Chemistry in Conventional Emulsion Polymerization

### 9.5.1 Reactive Latices

In the development of waterborne coatings, a main area of current research activities is the crosslinking of the polymer film. Traditionally, solvent-based coatings yield a crosslinked film after the drying process, whereas waterborne coatings result in a thermoplastic polymer film. A result of this is that the solvent resistance of solvent-based coatings is superior to that of waterborne coatings.

It is well known that the process of cohesive strength development in a waterborne polymeric coating consists of three main mechanisms (Daniels, 1991):

- 1) molecular interdiffusion of polymer chains from one particle into another,
- 2) interfacial crosslinking,
- 3) residual crosslinking.

This process of cohesive strength development is the final stage in the complex process of film formation. The two preceding stages are the evaporation of water and the coalescence of the polymer particles. These two stages have been investigated extensively, and a few different models have been proposed to describe these physical processes. In this section, we will mainly focus on the third stage of film formation, i.e., the cohesive strength development.

The first process of interest in the cohesive strength development is the interdiffusion of polymer chains. It is well known that the diffusion of polymer chains in a polymer matrix is strongly dependent on the molar mass of the chains. In terms of development of the cohesive strength, two opposing effects can be recognized:

- 1) Polymer with a relatively low molar mass ensures facile diffusion of chains from

one particle into the other after coalescence of the particles in the film-formation process. However, the effect of this interdiffusion on the strength development is not very large.

- 2) Polymer with a higher molar mass is hindered in its diffusion to a larger extent. However, the contribution of this diffusion process to the development of the cohesive strength is much larger than for low molar mass polymer.

The crosslinking method determines to some extent the requirements with respect to polymer–polymer interdiffusion. Two examples will be given below. One consists of a polymer that is to be crosslinked by a low molar mass crosslink agent. The other consists of two different polymers containing complementary reactive groups. Terms like interfacial crosslinking followed by residual crosslinking apply to the former of these examples, but not really to the latter.

#### 9.5.1.1 Crosslinking of Polymers by Low Molar Mass Crosslink Agents

The most elementary form of a crosslinking waterborne coating is where the emulsion polymer contains functional groups that are crosslinked in a reaction with a low molar mass crosslink agent. The crosslink agent will generally be added to the latex, immediately prior to application on the substrate. This type of system is referred to as a two-component coating for obvious reasons. In general, the crosslink agent will reside in the aqueous phase. Diffusion of the crosslink agent into the polymer particles is crucial in order to obtain a homogeneously crosslinked film. One of the concerns here is that, upon coalescence of the particles, a relatively high concentration of crosslink agent is present at the interface between the particles. This may result in a densely cross-

linked film at the interface, which greatly reduces the mobility of polymer chains across the interface, and may result in inhomogeneous crosslinking. In the previously indicated scheme, the third step, i.e., residual crosslinking, is hindered to some extent. One solution to this problem is the homogeneous distribution of crosslink agent throughout the polymer phase. In the regular systems this will result in crosslinking of the polymer particles before film formation. These crosslinked particles will not be able to undergo film formation, hence an inferior quality coating will be achieved. However, when the crosslinking reaction is intrinsically slow but its rate can be enhanced by some catalyst, this problem may be solved. In the area of microlithography, a possible solution is found in the use of photo acid generators (PAGs). PAGs are compounds that upon irradiation with light undergo a photochemical reaction, releasing an acid. Generally, this reaction leads to the production of protons. These protons easily diffuse in the polymer phase and may catalyze a reaction, as in the crosslinking reaction of the polymer with a low molar mass crosslinking agent (Verstegen, 1998). The approach where PAGs are used to crosslink the polymer film has two main advantages:

- 1) Homogeneous crosslinking may be achieved on the scale of a particle, since the actual crosslink agent can be homogeneously distributed throughout the particles.
- 2) Homogeneous crosslinking may be achieved on the scale of the thickness of the polymer film. In particular, in the case of UV curing, the effect of pigments on the homogeneity of the crosslink density can be quite dramatic. Extensive light scattering by the pigment particles may cause the lower part of the polymer film not to be irradiated at all. The protons re-

leased from the top layer of the film, however, will ensure the crosslinking of the lower layers as well.

One additional aspect concerning the homogeneity of the crosslinked network is the homogeneity of the polymer phase. Copolymers prepared by radical polymerization in general and emulsion polymerization in particular may exhibit inhomogeneity in their chemical composition distribution. There are two main reasons why this phenomenon occurs:

- 1) Composition drift caused by differences in the reactivities of the monomers applied, and
- 2) differences in water solubility, which may result in two types of polymer chains, one rich in the hydrophobic monomer, the other rich in the hydrophilic one (Noel et al., 1993).

One of the common functional monomers to induce crosslinking is 2-hydroxyethyl methacrylate (HEMA). This is a highly water soluble monomer compared to typical comonomers applied in waterborne coatings [butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate]. This large difference in water solubility results in strong variations of the comonomer ratio between the different phases of the polymerization mixture. To overcome this potential micro inhomogeneity problem, the use of other hydroxy functional monomers can be considered. The first obvious candidates are other  $\omega$ -hydroxyalkyl methacrylates, and more specifically 3-hydroxypropyl methacrylate (HPMA) and 4-hydroxybutyl methacrylate (HBMA). The reactivity ratios of HEMA, HPMA, and HBMA in their copolymerization with styrene are listed in Table 9-5. Presently, the commercial availability of these monomers is a major drawback. However, from a product quality point of

**Table 9-5.** Terminal model reactivity ratios for the copolymerizations of hydroxyalkyl methacrylates with styrene.

Comonomer	$r_H$	$r_{STY}$
HEMA <sup>a</sup>	0.48	0.27
HPMA <sup>b</sup>	0.256	0.161
HBMA <sup>b</sup>	0.159	0.103

<sup>a</sup> Schoonbrood (1994); <sup>b</sup> Versteegen (1998).

view, these monomers appear to be very promising. This may result in an increase in future production volume of these monomers.

### 9.5.1.2 Crosslinking Between Polymers with Complementary Reactive Groups

Polymer particles in a latex are stabilized from coagulation by the presence of surfactants on their surface. This means that polymer from one particle will never be in contact with polymer from another particle. Now, if we speak about reactive groups built in those polymers, they would be separated from polymer from other particles by the same mechanism. This characteristic feature can be used to let copolymers with complementary reactive groups coexist in one latex. This should be possible as long as a single particle contains only one functionality (Geurts, 1997).

Upon film formation, the particles all come into close contact. Eventually they coalesce and polymer–polymer interdiffusion as well as reaction can take place. In order to obtain a homogeneously crosslinked film, interdiffusion needs to take care of complete randomization on a molecular level in the polymer film. The initial strict separation between polymers with different functionalities needs to vanish completely. While this process is taking place, chemical reaction between the functional groups com-

mences. As mentioned before, the diffusion of polymer chains is related to its molar mass. This means that as soon as a polymer chain links to another one, its molar mass increases, and consequently its diffusion coefficient decreases. After a few reactions on one polymer chain, this chain will become virtually immobile. This means that there is a serious risk that the interface between adjacent polymer particles (carrying complementary reactive groups) will turn into a barrier for polymer diffusion shortly after coalescence of the particles takes place. The result of this would be a random structure of crosslinked walls separating the two types of copolymer with uncrosslinked material on both sides of the wall. It is clear that this problem is harder to solve than in the previous example, where diffusion of a mobile catalytic species is sufficient to overcome the inhomogeneous crosslinking. In the present case, the only way to ensure homogeneous crosslinking is to optimize the ratio of the diffusion rate and the rate of the chemical (crosslinking) reaction.

In order to test the system with complementary reactive groups, two mixed latices were investigated (Geurts, 1997):

- 1) Epoxy-functional (glycidyl methacrylate containing) copolymer with amino-functional (aminoethyl methacrylate containing) copolymer.
- 2) Acetoacetoxy-functional copolymer with amino-functional copolymer.

Measurements of the crosslinking rate indicate that the latter system has by far the highest rate. Recent conclusive results indicate that the epoxy–amine reaction is better suited for the purpose of crosslinking in a waterborne coating. Its rate of crosslinking enables better randomization of the polymer chains by diffusion, before the chemical reaction immobilizes the system.

### 9.5.2 Reactive Surfactants

An often unwanted effect of low molar mass surfactants is their migration to interfaces. In particular, in those cases where latexes are used in coating applications, this may lead to sticky surfaces and/or poor adhesion of the coating (Dickstein, 1986). In order to circumvent this disadvantage, reactive compounds may be used as surfactants (Kusters, 1994). These reactive surfactants are in some way incorporated in the polymer. This covalent binding to the polymer chain prevents migration during application or the lifetime of the coating.

Different possibilities exist to make the surfactant reactive in a free-radical polymerization process. The names of the compounds indicate the type of functionality that is incorporated:

- 1) inisurf, a surfactant with an initiator functionality,
- 2) surfmer, a surfactant that reacts as a comonomer in the polymerization,
- 3) transsurf, a surfactant that contains a moiety susceptible to chain transfer.

Each of the three techniques has certain advantages and disadvantages. A general concern is the even distribution of reactive surfactants over the polymer chain. For example, in the case of a surfmer, favorable reactivity ratios are required to prevent the formation of polymer with a large composition drift. Homopolymerization of the surfmer is unwanted due to the increased moisture sensitivity of this material. Similarly, for transsurfs it is necessary for the chain transfer constant to have a value close to unity, so that its consumption rate is nearly equal to that of the monomer. In any other case, unwanted side effects may arise. Too fast consumption leads to a too low level of surfactant in the latter stages of the polymerization, and thus potentially to instability of

the latex. Too slow consumption results in residual transsurf at the end of the polymerization, and thus to similar problems, as observed with ordinary surfactants.

In the case of inisurfs it is often found that the initiator efficiency is poor. This is mainly ascribed to the formation of two radicals in close proximity, which favors bimolecular termination. This problem may be circumvented by the application of surfactants containing a hydroperoxide moiety which can be dissociated with a redox mechanism. However, this approach is rather cumbersome from a synthetic point of view.

## 9.6 Unconventional Emulsion Polymerization

There are many unique polymerization processes that share a common heritage with emulsion polymerization, but they are often not recognized as such. It is the purpose of this review to describe some of these emulsion polymerization-like processes and their products. Some further definition is in order: Unconventional emulsion polymerizations can be described as those processes whereby the product is a polymer latex that physically resembles latexes from emulsion polymerization *and* cannot be grouped into any other recognized heterogeneous polymerization technique. In many cases the reason why a process is not recognized as an emulsion polymerization is that the polymerization does not occur via a free-radical process. In the following sections unconventional emulsion polymerizations that take place according to four distinct types of polymerization mechanism will be discussed. All of these cases have examples where polymer particles are produced, and in many ways these processes can be described as unconventional emulsion polymerizations. The relevant systems are free-

radical polymerization, ionic polymerization, transition metal-catalyzed polymerization and enzyme-catalyzed polymerization. For a more detailed review of unconventional emulsion polymerizations, see Kurja et al. (1997).

### 9.6.1 Unconventional Free-Radical Emulsion Polymerization

There is an important category of free-radical emulsion polymerizations where the hydrophobic polymer does not dissolve in its own monomer (Guyot, 1989; Putman, 1989; Murray and Piirma, 1993; McCarthy et al., 1986) or is only sparingly soluble in its own monomer (Guyot, 1989). Some examples of these kinds of polymerization are the emulsion polymerization of fluorinated monomers, e.g., tetrafluoroethylene (TFE) (Putnam, 1989; Murray and Piirma, 1993), and acrylonitrile (McCarthy et al., 1986). The polymers formed by these polymerizations all have significant industrial importance, particularly as engineering polymers, e.g., Teflon, acrylonitrile–butadiene–styrene rubber (ABS). The fact that these polymers do not dissolve in their own monomers causes phase separation between monomer and polymer at very low conversions during the polymerization process. Due to this phase separation, the locus of polymerization is not the interior of the polymer particles, simply because there is no monomer in the interiors, but polymerization mainly occurs at the surface of the polymer particles (Murray and Piirma, 1993; McCarthy et al., 1986). Evidence for this behavior is that the rate of polymerization is proportional to the total surface area of the polymer particles (Murray and Piirma, 1993). Therefore a kinetic treatment of these polymerization processes necessarily considers the surface area of the polymer particles rather than the

polymer particle volume, as is usually the case in emulsion polymerization.

Another unusual free-radical polymerization of vinyl monomers utilizes ultrasound to both emulsify monomer and to create free radicals (Cooper et al., 1995). The ultrasound (at 20 kHz) acts on the water to create hydrogen and hydroxyl-initiating radicals, an initiating system that bears resemblance to many radiation-induced polymerizations. The first-claimed emulsion polymerizations by ultrasound were those of butyl acrylate and vinyl acetate (Cooper et al., 1995). In most cases it was observed that the particle sizes obtained by ultrasound initiation are smaller than those of equivalent chemically initiated polymerizations, although they may be dependent upon the energy input. It is interesting to note that this approach to initiation is a possible alternative to radiation-induced initiation in (pulsed) kinetic studies of (emulsion) polymerization mechanisms.

The preparation of conducting polymers in an emulsion is generally via an oxidative coupling mechanism in which the active polymerizing species are free radicals. This polymerization process, which is distinct from radical (vinyl, acrylic, etc.) chain polymerization, is described in detail elsewhere (Lux, 1994). As a result of their conjugated backbones, conducting polymers are intrinsically intractable polymers, making them very hard to process. Preparing these polymers in an emulsion may overcome many of these processing problems. Examples of conducting polymers which have been produced in an emulsion are polyacetylene, polypyrrole (PPy), and polyaniline (PANI) (Edwards et al., 1983; Armes et al., 1987; Arnes and Vincent, 1988; Österholm et al., 1993). The literature on the oxidative polymerization of aniline in an aqueous medium describes both dispersion and emulsion types of polymerization, each with different



types of stabilizer (Österholm et al., 1993, 1994; Banerjee et al., 1994; Stejskal, 1993). Depending on the kind and concentration of surfactant/polymeric stabilizer, polymer particles ranging from 300 to 400 nm can be obtained. In the case of the polymerization of pyrrole in water, the size of the formed polymer particles can be adjusted over a relatively broad range, i.e., between 10 and 250 nm, depending on the oxidizing agent, stabilizer, and so on (Armes et al., 1987; Cawdery et al., 1988; Eisazadeh et al., 1994).

### 9.6.2 Ionic Emulsion Polymerization

Numerous studies have been conducted concerning the polymerization of siloxanes (Andranov et al., 1979; Sigwalt and Stannett, 1990; Andrianov and Dabagora, 1960), but have focused mainly on bulk polymerization. Emulsions of polysiloxanes have attracted great attention since the 1980s due to the fact that they can be utilized in surface coatings. Hyde and Wehrly (1959) described the emulsion polymerization of permethylcyclsiloxanes, which proceeds via an anionic polymerization mechanism involving a basic catalyst with a cationic surfactant. Weyenberg et al. (1969) developed an analogous acid-catalyzed anionic emulsion polymerization, which employs dodecylbenzenesulfonic acid (DBSA) as the catalyst and surfactant. The cationic polymerization can be compared with a conventional free-radical emulsion polymerization: The cationic polymerization involves monomer, water, surfactant, and catalyst, and the particle size of the resulting polymer dispersion is normally much smaller than that of the initial monomer droplets. Polydimethylsiloxane emulsions with particle diameters of 50–500 nm can be obtained on heating aqueous dispersions of permethyl cyclsiloxanes with dodecylbenzenesulfonic acid

at 50–100°C. There are two major differences between cationic polymerizations of siloxane and conventional emulsion polymerizations. Firstly, there is a distinct difference between the catalyst used, i.e., a cationic catalyst instead of a free-radical one. Secondly, there is a different role of water in the polymerization mechanism. In the case of the free-radical emulsion polymerization, water serves as an inert suspending medium. However, in the siloxane polymerization, water serves as a reactant and consequently affects the molar mass of the polymer.

### 9.6.3 Transition Metal Catalyzed Emulsion Polymerization

Generally speaking, transition metal catalyzed polymerization cannot be performed in aqueous media, since water destroys active catalyst complexes. However, there are a few monomers that have been polymerized in pure water via transition metal catalyzed reactions.

Palladium-based catalysts can be used for the polymerization of norbornene (Mehler and Risse, 1992) and the copolymerization of ethylene and carbon monoxide (Drent et al., 1991; Jiang and Sen, 1994). However, there are only two reports of these polymerizations in aqueous media, namely, the oligomerization of norbornene (Eychenne et al., 1993) and the alternating copolymerization of ethylene and carbon monoxide (Jiang and Sen, 1994). In the case of the oligomerization of norbornene, a 'micro-latex' was obtained with an average particle diameter of approximately 10 nm with  $\text{PdCl}_2$  as the catalyst and sodium dodecylsulfate as the surfactant. In 1969, Rinehart et al. (1962) and Canale et al. (1962) independently reported on the rhodium-catalyzed emulsion polymerization of butadiene to a high *trans*-1,4

polymer utilizing sodium dodecylbenzenesulfonate as the surfactant. Almost ten years later, Entezami et al. (1977) showed that *trans*- and *cis*-1,3-pentadiene can be polymerized in an emulsion using  $\text{RhCl}_3$  as the catalyst and sodium dodecylbenzenesulfonate as the surfactant. Unfortunately, these authors did not mention polymer particle sizes. Finally, ethylene can also be polymerized in an emulsion (Stryker et al., 1969) using a rhodium-based catalyst.

The first true ring-opening metathesis polymerization in an emulsion of different norbornenes, using transition metals as catalysts, was reported by Rinehart and Smith (1965). These ROMP polymerizations were carried out with  $(\text{NH}_4)_2\text{IrCl}_6$  and  $\text{RuCl}_3$  as the catalysts, plus a reducing agent, and different surfactants depending on the monomer polymerized. One of the major problems encountered with these polymerizations is the low yield of polymer. Several years ago, Novak and Grubbs (1988a, b) reported on the ROMP of certain heteropolycyclic alkenes (7-oxanorbornene derivatives) in pure water using ruthenium salts. Feast and Harrison (1991) investigated the aqueous emulsion ROMP of *exo,exo*-2,3-bis(methoxymethyl)-7-oxanorbornene (BMM-7-ON) using ruthenium, iridium, and osmium chloride as the precursors of the active catalysts. Only very recently, Lu et al. (1993) were the first to report the aqueous dispersion (emulsion) polymerization of BMM-7-ON, using  $\text{RuCl}_3$  as the catalyst and a polyethylene oxide–polypropylene oxide tri-block surfactant. With increasing surfactant concentration, the diameter of the polymer particles became smaller, which is a general observation in emulsion polymerization. The particle diameters were typically in the range of 40–60 nm.

#### 9.6.4 Enzyme-Catalyzed Emulsion Polymerization

The initial motivation behind the emulsion polymerization of butadiene in the late 1920s was the search for a substitute for natural rubber. The appellation “latex” is used for the extract tapped from the rubber tree. This is also used to describe the product of a synthetic emulsion polymerization. Natural rubber is one of three biopolymers formed by an enzyme-catalyzed polymerization, which is recognizable as an emulsion polymerization. Bacterial polyhydroxyalkanoates and cellulose are the other two.

Natural rubber is synthesized by a wide variety of plants. The botanic rationale for this synthesis is still a mystery. The biosynthesis of natural rubber has been studied extensively in the past (Backhaus, 1985; Archer and Audley 1987; Tanaka, 1989; Paterson-Jones et al., 1990), and the basic polymerization reactions have been defined. However, the full mechanism of formation of the rubber particles has still not been elucidated, although some suggestions have been made (Archer and Audley, 1987; Paterson-Jones et al., 1990; Hager et al., 1979). The formation of *cis*-poly-1,4-isoprene is a heterogeneous polymerization where the polymerization mainly occurs at the surface of the rubber particles. The propagating rubber transferase molecule is mainly situated at the surface of a rubber polymer particle (Cornish, 1993; Lynen, 1969). The sizes of the rubber polymer particles can vary from 10 nm to several micrometers (Paterson-Jones et al., 1990).

Poly-(*R*)-3-hydroxyalkanoates (PHAs) are linear biopolyesters produced by a wide variety of bacteria as a reserve of carbon and energy (Anderson and Dawes, 1990). Very recently, De Koning and Maxwell (1993) drew an analogy between the conventional

emulsion polymerization process and the biosynthesis of PHAs. Based on this, Kurja et al. (1994, 1995) made a more quantitative description of the accumulation of poly-(*R*)-3-hydroxybutyrate (PHB) in *Alcaligenes eutrophus*. PHAs are synthesized via a polycondensation reaction (Anderson and Dawes, 1990). However, the molar mass of the polymer formed during the early stages (low conversions) of the accumulation process is high, typically of the order of  $10^5 \text{ g mol}^{-1}$  (Anderson and Dawes, 1990), indicating a chain mechanism of polymerization (Kurja et al., 1994, 1995). The biosynthesis of PHB can be understood in terms of the kinetic processes of initiation, propagation, and chain transfer, and the effect of polymer particle size on these. The polymerization process takes place mainly at the surface of the granules (read: polymer particles), which is also observed for the emulsion polymerization of monomers that are poor solvents for their own polymers (see Sec. 9.6.2). Furthermore, the colloidal aspects of the formation of PHB polymer particles can be explained by the homogeneous nucleation mechanism, well known in conventional emulsion polymerization processes.

It is apparent that the mechanism of rubber formation displays similarities to that of PHB. For this reason it is likely that useful comparisons can be made between the mechanisms of conventional emulsion polymerization and the emulsion polymerization producing natural rubber, particularly in a fashion as already applied to PHB. A very important aspect of these biological emulsion polymerizations is the fact that they produce unique and different polymer latexes, i.e., a polyolefin, a polyether, and a polyester, all from renewable resources. This may be of future interest in polymer science, especially as oil reserves are depleted.

### 9.6.5 Concluding Remarks

If the product of a polymerization is a latex, then the process of polymerization can be considered either in part or in full as an emulsion polymerization. The advantage of doing so is that the physical chemistry of emulsion polymerization combined with the appropriate polymer chemistry allows, in many cases, fuller understanding of the *unconventional* emulsion polymerization. In the last few sections, a brief survey of those heterogeneous polymerization processes that can be considered as unconventional emulsion polymerizations has been given. Since it is likely that many other unconventional emulsion polymerizations exist, the purpose of this section is to only give an introduction to this field. The polymerizations described have mainly not been the subject of in-depth kinetic studies, which is reflected in the summaries of their processes. Although analogies have been drawn between unconventional and conventional emulsion polymerizations, there are still many features of the former that cannot be understood by such analogies. There is clearly scope for much work in this field.

## 9.7 Applications

Polymer colloids find their way into many industrial products and applications, such as synthetic latices [styrene–butadiene copolymers, acrylonitrile–butadiene rubbers, chloroprene rubbers, acrylic (co)polymers, vinyl acetate (co)polymers, vinyl chloride (co)polymers, synthetic *cis*-polyisoprene, and butyl rubber], paints, (paper) coatings, adhesives, biomedical and pharmaceutical applications, impact modifiers for thermoplastic matrices, and conducting polymers such as polyaniline.

### 9.7.1 Paints

Emulsion polymers are widely used in waterborne paints (Lambourne, 1987). The latices are prepared by emulsion polymerization of acrylic, methacrylic, or vinyl monomers. Other ingredients are pigments (usually organically modified), colloidal stabilizers (usually a mixture of ionic and nonionic surfactants), and a large quantity of additives like anti-foaming agents, thickeners, etc.

Waterborne paints can be found in such application fields as decorative coatings, automotive coatings, and can coatings. Challenges in the field of developing waterborne coatings are for example to reduce the amount of coalescing agents necessary to obtain good film formation. These coalescing agents have to evaporate out of the film to obtain a  $T_g$  high enough to prevent blocking, and are therefore environmentally hazardous. One way to overcome the need for coalescing agents is to increase the  $T_g$  by crosslinking the latex after film formation (see Sec. 9.5.1).

The water resistance of films resulting from waterborne paints is sometimes not optimal because of the surfactants still present in the dry film and the poor interaction between pigment particles and matrix polymer. The application of reactive surfactants and the modification of pigment particles by encapsulation with polymer (see Sec. 9.4.2.2) are two topics of current research to improve the water resistance. Furthermore, the use of polymer particles with core-shell morphologies (see Sec. 9.4.2) can be advantageous for the film's properties.

### 9.7.2 Paper Coatings

One of the largest users of latexes is the paper coating industry. The main objectives

of coating papers and paper boards are to improve their aesthetic appearance and printability. The coatings consist of pigments, binders, and water, together with minor quantities of functional ingredients such as defoamers, flow modifiers, and fluorescent whitening agents. Various types of soft latexes, such as styrene-butadiene (S/B), styrene-butylacrylate (S/BA), and polyvinyl acetate (PVAc) latexes are widely used as binders in paper coatings. Their function is to fix the pigment particles to the paper surface. The nature and level of binder present will influence the coating mix rheology and modify the printability characteristics. Future research is focused on super-binder, super-runability binder, high gloss and easy finishing binder coating structure control, and better fundamental understanding of coatings, drying, finishing, and printing processes (Lee, 1996).

### 9.7.3 Adhesives

The pressure-sensitive adhesives (PSAs) market is dominated by solvent-based materials. The change in the environmental and economic climate offers opportunities for water-based PSAs. However, there are some problems in emulsion PSA that need to be overcome. The shortcomings of emulsion PSAs are: (1) lower peel adhesion than corresponding solvent PSAs, (2) sensitivity to water/humidity, (3) colloidal stability during pumping and coating, (4) foaming during coating, and (5) poor wetting of low surface energy substrates. These problems are mainly due to the heterogeneous nature of emulsion polymerization, which affects the copolymer composition. Also, the surfactants, wetting agents, and defoamers affect the PSA's properties.

In PSA synthesis, polar monomers are used, such as acrylic acid, methacrylic ac-

id, acrylamide hydroxyethyl methacrylate, glycidyl methacrylate, *t*-butyl acrylamide, dimethylaminoethyl methacrylate, and maleic anhydride. In heterogeneous emulsion copolymerization with these polar monomers, water solubility of these monomers is high and therefore heterogeneous copolymers are formed. The copolymer's composition is often different from that of its solvent-polymerized counterpart. Differences in the true copolymer composition result in totally different PSA performance. Therefore the emulsion polymerization reaction engineering is very important for the control of these compositional effects (Yanagihara, 1983).

#### 9.7.4 Biomedical and Pharmaceutical Applications

The use of polymer colloids for biomedical and pharmaceutical applications is very interesting. Examples of such polymer colloids are the polystyrene latexes used in the medical field (Singer, 1987; Singer and Plotz, 1996). Furthermore, extended research on free-radical heterogeneous polymerization has led to well-defined polymer nanoparticles suitable for numerous applications in medicine and biology. There are still many challenges to develop new kinds of nanoparticles with innovative properties (Pichot et al., 1996), such as:

- polymer particles with a specific structure, mimicking various phenomena involved in living systems,
- reactive particles with better control of the accessibility, reactivity, and surface density of the functional groups,
- very small nanoparticles (below 60 nm), as produced by microemulsion or micellar polymerization processes, taking into account the extensive understanding in the physiochemistry of these dispersed systems,

- hydrophilic and stimuli-responsive particles (“smart material”) for various biotechnology (sensors) and biology purposes.

Not only is the polymer synthesis very important, but the characterization techniques cannot be neglected in this field of research either. There are many problems in defining the interactions with biologically active macromolecules or drugs. Many and complex questions remain with respect to the mechanism of interactions and their effects on the performance of the biomolecule activity.

#### 9.7.5 Impact Modifiers

Amorphous thermoplastics (e.g., polystyrene and polymethyl methacrylate) and crosslinked resins (e.g., epoxy resins and polyester resins) are very brittle and to improve these fracture properties, rubbers are dispersed in the polymer matrix in discrete micrometer or sub-micrometer size domains. The conventional route to prepare rubber-toughened plastics is the formation of toughening particles by phase separation from the matrix material. This can lead to major difficulties in the simultaneous control of matrix properties and toughening particle size, morphology, and chemistry. However, when the rubber is made by emulsion polymerization, the preformed particles (i.e., pre-defined diameter, morphology, and chemical composition) can be easier and more finely dispersed in the polymer matrix and will therefore be less dependent on the processing parameters. An overview of the preparation and use of emulsion polymer particles for the toughening of plastics is given by Lovell (1995). These rubber particles are mostly prepared by seeded emulsion polymerization. The shell of the composite particle improves the compatibility of

the rubber in the polymer matrix (Aerdt et al., 1997). Recently, Ruckenstein and Hangquan (1996) published a new procedure for toughening polymers, where the composites are prepared via the heterogeneous cross-linking of concentrated emulsions.

## 9.8 References

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## General Reading

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**Appendix I.** Propagation rate coefficients and activation parameters: Pulsed laser polymerization combined with size exclusion chromatography (PLP-SEC) is the most accurate method to date to obtain propagation rate coefficients, as concluded by the IUPAC working party on kinetics and modeling of polymerization reactions [see, for example, Buback et al. (1995)]. In the table a compilation of the latest (August, 1996)  $k_p$  values and activation parameters is given, which was obtained with the PLP-SEC method (see Table p. 317). ►

**Appendix II.** Water solubilities of monomers: The water solubility of monomers applied in emulsion polymerization is very important, because in copolymerizations it will have an effect on the composition drift. Furthermore, monomers with a high water solubility can also given solution polymerization, next to emulsion polymerization.

Monomer	$T$ (°C)	$C_w^{\text{SAT}}$ (mol dm <sup>-3</sup> )	Reference
Acrylamide	— <sup>b</sup>	vs <sup>e</sup>	<i>Polymer Handbook</i> (1989)
Acrylic acid	— <sup>b</sup>	∞ <sup>f</sup>	<i>Polymer Handbook</i> (1989)
Acrylonitrile	— <sup>b</sup>	s <sup>c</sup>	<i>Polymer Handbook</i> (1989)
1-3 Butadiene, 1 atm <sup>g</sup>	0	$3.8 \times 10^{-2}$	Saltman (1965)
1-3 Butadiene, 1 atm <sup>g</sup>	50	$6 \times 10^{-3}$	Saltman (1965)
1-3 Butadiene, sat. <sup>a</sup>	50	$3.7 \times 10^{-2}$	Reed and McKetta (1955)
1-3 Butadiene, sat. <sup>a</sup>	70	$4.3 \times 10^{-2}$	Reed and McKetta (1955)
1-3 Butadiene, sat. <sup>a</sup>	100	$5.7 \times 10^{-2}$	Reed and McKetta (1955)
Butyl acrylate	50	$6.4 \times 10^{-3}$	Capek et al. (1984)
Butyl methacrylate	50	$2.5 \times 10^{-3}$	Halnan et al. (1984)
Hydroxy ethyl methacrylate	50	∞ <sup>f</sup>	Van Es et al. (1997)
Hydroxy propyl methacrylate	50	0.382	Van Es et al. (1997)
Hydroxy butyl methacrylate	50	0.17	Van Es et al. (1997)
Hydroxy hexyl methacrylate	50	$3.7 \times 10^{-2}$	Van Es et al. (1997)
Hydroxy octyl methacrylate	50	$5 \times 10^{-3}$	Van Es et al. (1997)
Methacrylic acid	— <sup>b</sup>	s <sup>c</sup>	<i>Polymer Handbook</i> (1989)
Methyl acrylate	50	$6.1 \times 10^{-1}$	Van Doremale et al. (1992)
Methyl methacrylate	50	$1.5 \times 10^{-1}$	Ballard et al. (1984)
Styrene	50	$4.3 \times 10^{-3}$	Lane (1946)
Vinylacetate	50	$5.0 \times 10^{-1}$	Hawket (1974)
Vinyl chloride	— <sup>b</sup>	ss <sup>d</sup>	<i>Polymer Handbook</i> (1989)

<sup>a</sup> At saturation pressure of 1-3 butadiene; <sup>b</sup> — temperature not specified, ambient; <sup>c</sup> s soluble; <sup>d</sup> ss slightly soluble; <sup>e</sup> vs very soluble; <sup>f</sup> ∞ miscible with water; <sup>g</sup> 10<sup>5</sup> N m<sup>-2</sup>.

Appendix I

Monomer	Solvent	A (L mol <sup>-1</sup> s <sup>-1</sup> )	E <sub>a</sub> (kJ/mol)	10°C <sup>c</sup>	25°C <sup>c</sup>	30°C <sup>c</sup>	40°C <sup>c</sup>	50°C <sup>c</sup>	60°C <sup>c</sup>	70°C <sup>c</sup>	Reference
Acrylamide	water, pH = 1		20		16 000						Pascal et al. (1990)
Methacrylamide	water, pH = 1		20		1 000						Pascal et al. (1990)
BA	bulk	2.51×10 <sup>7</sup>	20								Meuts et al. (1994)
BA <sup>a</sup>	THF/toluene	1.66×10 <sup>7</sup>	17.27								Lyons et al. (1996)
BA <sup>a</sup>	bulk	1.8×10 <sup>7</sup>	17.4								Beuermann et al. (1996)
n-BMA	bulk, 1000 bar <sup>d</sup>	7.28×10 <sup>6</sup>	22.9	10 800	15 600	17 500	21 800	26 800	32 500	39 000	Beuermann et al. (1996)
n-BMA <sup>a</sup>	bulk	3.44×10 <sup>6</sup>	23.3	434 !U	708	824	1 100	1 450	1 870	2 380	Bergert et al. (1995a)
n-BMA <sup>a</sup>	bulk	1.81×10 <sup>6</sup>	20.55		274						Davis et al. (1990)
i-BMA <sup>a</sup>	bulk	2.51×10 <sup>7</sup>	27.7	289	454	523	676	857	1 108	1 394	Hutchinson et al. (1995a)
i-BMA <sup>a</sup>	bulk	2.47×10 <sup>6</sup>	21.53	252	417	496	633	798	1 040	1 336	Pascal et al. (1993)
Butadiene	chlorobenzene	8.05×10 <sup>7</sup>	35.71	20.8	44.6	56	85	138	204	295	Hutchinson et al. (1995a)
Chloroprene	bulk	1.95×10 <sup>7</sup>	26.63	235	447	485	673	988	1 300	1 720	Delbert et al. (1992)
DA	bulk	1.09×10 <sup>7</sup>	15.8	17 660	18 600	22 113	25 300	30 500	36 400	43 000	Hutchinson et al. (1993)
DMA	bulk, 100 bar <sup>d</sup>	3.44×10 <sup>6</sup>	21.72	339	538	622	819	1 060	1 350	1 700	Beuermann et al. (1996)
DMA	toluene	2.93×10 <sup>5</sup>	16.19	300	427	452	601	796	848	1 010	Hutchinson et al. (1995b)
EHA	bulk			13 180	18 030						Davis et al. (1990)
EMA	bulk	1.50×10 <sup>6</sup>	20.46		258						Beuermann et al. (1996)
EMA <sup>a</sup>	bulk	3.65×10 <sup>6</sup>	22.89	206	356	400	590	676	939	1 160	Hutchinson et al. (1995a)
PMOS	toluene	5.90×10 <sup>5</sup>	23.0	33.7	52	64.2	85.9	113	146	186	Piton et al. (1990)
MA	bulk, 1000 bar <sup>d</sup>	3.61×10 <sup>6</sup>	13.9	9 860	13 300	14 600	17 400	20 500	24 000	27 700	Bergert et al. (1998)
MAA	methanol	0.6×10 <sup>6</sup>	17.7	326	477	536	671	828	1 009	1 215	Beuermann et al. (1997a)
MAN	bulk/benzene	2.69×10 <sup>6</sup>	29.7	8.9	16.8	20.5	29.9	42.5	59.3	81	Shipp et al. (1995)
MMA	bulk	2.39×10 <sup>6</sup>	22.18	193	311	360	470	621	769	989	Hutchinson et al. (1993)
MMA <sup>a</sup>	bulk	2.65×10 <sup>6</sup>	22.34	200	323	375	497	649	833	1 050	Beuermann et al. (1997b)
MMA	bulk	4.94×10 <sup>6</sup>	23.94		316			667			Bergert et al. (1995b)
MMA	toluene/					384					Beuermann et al. (1994a)
MMA	2-butanone										Davis et al. (1989)
MMA	bulk/ethylacetate/				294						
MMA	methanol										
MMA	bulk					364					Beuermann et al. (1994b)
MMA	bulk				313						Olaj and Schnöll-Bitai (1989)
<sup>1</sup> H <sub>8</sub> -MMA	bulk				270						Olaj and Schnöll-Bitai (1990)
<sup>2</sup> H <sub>8</sub> -MMA	bulk				342						Olaj and Schnöll-Bitai (1990)
S	bulk				77						Olaj and Schnöll-Bitai (1989)
S	toluene				79						Olaj and Schnöll-Bitai (1989)
S	bulk/methanol/				78						Davis et al. (1989)
S	ethylbenzene										
S	bulk	1.99×10 <sup>7</sup>	30.78	41.7	80.6	98.9	146	211	297	411	Davis et al. (1989)
S	bulk	3.04×10 <sup>7</sup>	31.48			116		248		490	Buback and Kuchta (1995)
S <sup>b</sup>	bulk	4.27×10 <sup>7</sup>	32.51	42.9	85.9	107	161	237	341	480	Buback et al. (1995)
Vinylacetate	bulk	2.7×10 <sup>8</sup>	27.82	1 935	3 420						Hutchinson et al. (1995a)
Vinylacetate <sup>a</sup>	bulk	1.49×10 <sup>7</sup>	20.39	2 580	3 990	4 570	5 910	7 540	9 460	11 700	Hutchinson et al. (1995b)

<sup>a</sup> Most recent values; <sup>b</sup> IUPAC values; <sup>c</sup> Values calculated from the Arrhenius parameters in italics; <sup>d</sup> ×10<sup>5</sup> N m<sup>-2</sup>.



# 10 Organic/Inorganic Hybrid Polymers

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## List of Symbols and Abbreviations

$a$	Mark-Houwink exponent
$h$	Planck constant
$l_p$	persistent length
$m$	number
$M_n$	number-average molecular weight
$M_w$	weight-average molecular weight
$n$	number
$P_n$	number-average degree of polymerization
$P_w$	weight-average degree of polymerization
$T_g$	glass transition temperature
$T_m$	melting temperature
$x, y, z$	number
$\epsilon$	extinction coefficient
$[\eta]$	intrinsic viscosity
$\lambda$	wavelength
$\nu$	frequency
$\sigma$	electric conductivity
$\tau_s$	electro-optic switching time
$\chi^{(2)}$	second-order nonlinear optical susceptibility
$\chi^{(3)}$	third-order nonlinear optical susceptibility
Ac	acetyl
acac	acetylacetonate(-o)
ADMET	acyclic diene metathesis
bpy	2,2'-bipyridine
Bu	butyl
BuLi	<i>n</i> -butyllithium
Cp	cyclopentadienyl
DMA	dimethylacetamide
DMSO	dimethylsulfoxide
ESR	electron spin resonance
Et	ethyl, C <sub>2</sub> H <sub>5</sub>
GPC	gel-permeation chromatography
IR	infrared
LAH	lithiumaluminumhydride, LiAlH <sub>4</sub>
LB	Langmuir-Blodgett
LED	light-emitting diode
M	metal
Me	methyl, CH <sub>3</sub>
Mt	metal
NMR	nuclear magnetic resonance
Nu	nucleophil

Ph	phenyl
ROP	ring-opening polymerization
SAXS	small-angle X-ray scattering
TEM	transmission electron microscopy
THF	tetrahydrofuran
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
TPFPB	tetrakis(pentafluorophenyl)borate
tppz	tetrapyridophenazine
UV	ultraviolet



## 10.1 Introduction

The overwhelming majority of synthetic macromolecules known today is characterized by a backbone that contains either only carbon or carbon in combination with a selection of nonmetallic heteroatoms like oxygen, nitrogen, sulfur, or phosphorus. This predominance of “organic polymers” is contrasted by a tremendous lack of well-defined organic/inorganic hybrid polymers, i.e., macromolecules where carbon does not play the key role in the backbone. Of course, there are plenty of well-known inorganic or organometallic chain molecules in inorganic and solid-state chemistry, but almost all of them are insoluble and infusible or decompose when heated or brought into contact with a potential solvent. Hence they are inaccessible for profound polymer analysis and, in general, not considered to be well-defined macromolecules. The obvious preference of organic polymers in today’s science and technology is mainly due to the fact that the exploitation of fossil carbon sources like oil, coal, or gas is cheap and convenient. Hence people preferred the development of organic to inorganic processes, and macromolecular science clearly became a part of organic rather than inorganic chemistry.

Research on soluble hybrid polymers has increased dramatically only in the last two decades. The search for novel synthetic challenges was one important reason for this development, but also the new interest in supramolecular chemistry and the need for new materials with exceptional properties helped induce this impressive catch-up process (Ciardelli et al., 1996; Manners, 1996; Mark et al., 1992). First, however, these efforts were hindered by the lack of appropriate organic/inorganic hybrid monomers and optimized reaction conditions, which would ensure homogeneous and quantitative con-

version of these monomers – radical or ionic chain polymerization of unsaturated monomers proved to be possible only in some specific cases – and the apparently easier step-growth processes were also problematic. Consequently, only low molecular weight products of irregular constitution became available in most cases. Fundamental progress has only been possible since the late 1980s when modern polymerization reactions were applied, such as ring-opening polymerization or transition metal catalyzed polycondensation reactions. These novel synthetic techniques – in combination with new concepts like using solubilizing side chains and dendritic growth – opened up access to an impressive variety of soluble hybrid polymers and hence revolutionized our knowledge about this fascinating class of macromolecular systems.

## 10.2 Scope and Structure

In this chapter, well-defined macromolecules are described whose chemical structure is represented by one of the three schematic drawings **A–C** shown in Fig. 10.1. Thus polymers with carbon-containing building blocks in the main chains are considered, if these organic blocks are (i) short and (ii) connected covalently or coordinatively to one another by (semi)metals (**A**, **B**). In contrast to this, systems **C** have a completely carbon-free main chain but bear organic substituents as side groups. On the other hand, macromolecules that have strictly carbon-free chemical structures (**D**) are disregarded here as well as all those macromolecule metal complexes in which (semi)metals are laterally attached to an otherwise purely organic polymer (**E–G**). The second prerequisite for considering a hybrid poly-

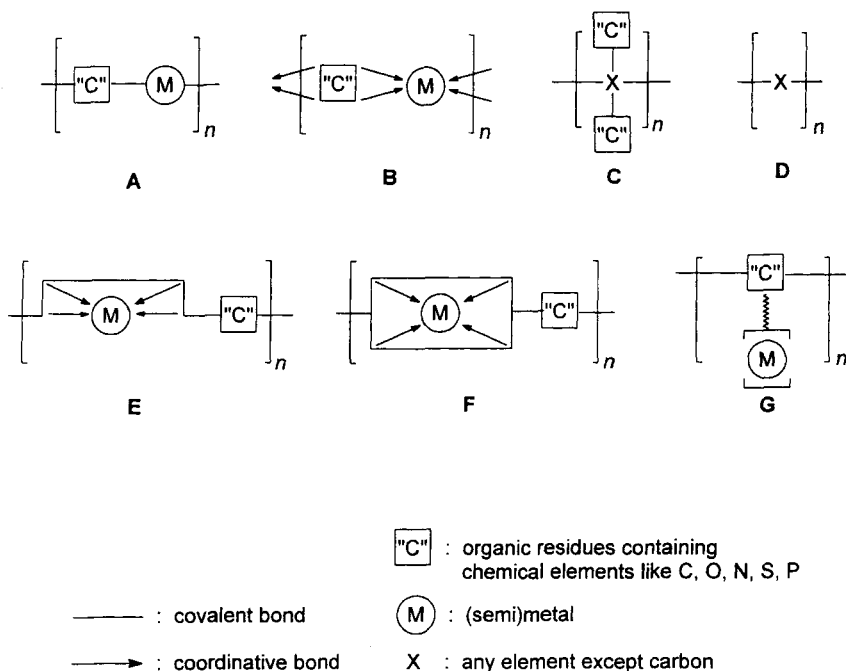


Figure 10-1.

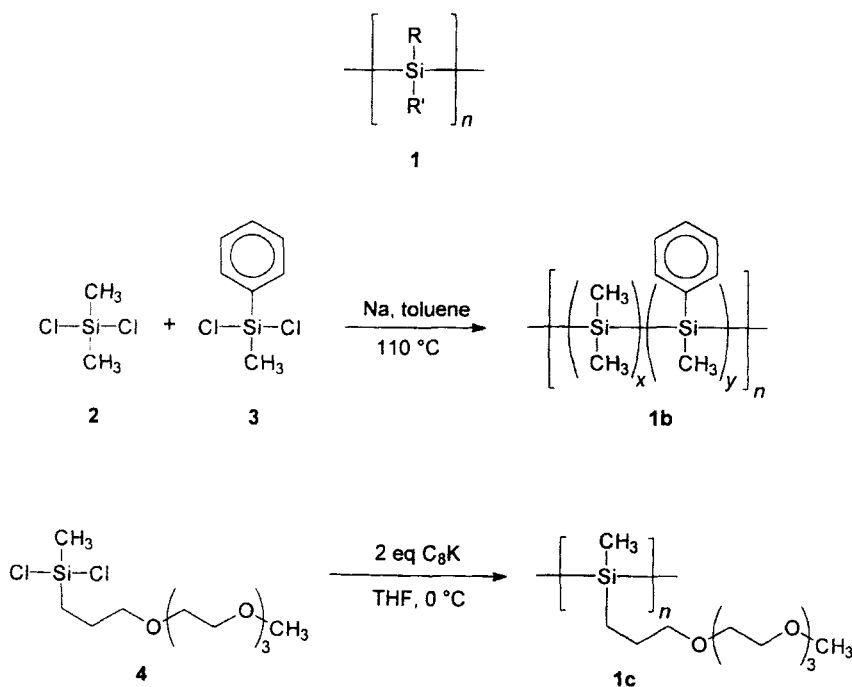
mer here is that it must be soluble and thus have a constitution and an average molecular weight that can be determined experimentally.

The following description of the individual hybrid polymer classes is divided into three parts. In the first part (Sec. 10.3), polymers are described that only have main group elements in their backbone, while the second part (Sec. 10.4) deals with polymers that additionally contain transition metals. In the third part (Sec. 10.5), some macromolecules are presented that contain stacked planar ring systems, irrespective of whether the main chains contain transition metals or not.

## 10.3 Polymers with only Main Group Elements in Their Backbone

### 10.3.1 Polysilanes

Polysilanes **1** (Scheme 10-1), i.e., polysilylenes, have a main chain that is made up entirely of silicon atoms. The two remaining valences at each silicon bear substituents  $R$ ,  $R'$ , which are typically organic (alkyl, aryl) but may also be H,  $\text{Me}_3\text{Si}$ , or others. Oligomeric silanes have been studied for more than 70 years (Kipping, 1924), but the belief that silicon has only a limited capability for catenation persisted until quite recently (Mark et al., 1992). In 1975, Yajima observed that the insoluble polydimethylsilane **1a** ( $\mathbf{a}$ :  $R = R' = \text{CH}_3$ ), as well as its cyclic oligomer  $(\text{Me}_2\text{Si})_6$ , transform into silicon carbide at high temperatures (Yajima



Scheme 10-1.

et al., 1975 a, b). This important finding initiated renewed attempts to make well-defined polymers **1** of high molecular weights available. Only three years later, West et al. showed that the introduction of some randomly distributed phenyl groups into polysilane homopolymers such as **1a** greatly reduces their crystallinity and thus increases their solubility and lowers their melting temperatures: Soluble and thermoplastic polysilane copolymers **1b** became available via Wurtz coupling of mixtures of **2** and **3** with sodium metal in boiling toluene (Mazdyasni et al., 1978; West et al., 1981).

Since then, many other well-defined polysilanes **1** of high molar mass ( $M_n > 10^5$ ) have been prepared using the Wurtz coupling. Nevertheless, the classic Wurtz reaction (Burkhard, 1949) also has some specific disadvantages, i.e., low tolerance towards functional groups, low yields, and bimodal or even multimodal molecular weight distributions in the products. The lat-

ter observation has been interpreted as a result of the complex reaction mechanism involving radical, anionic, and silylene intermediates (Odian, 1991; Gauthier and Worsfold, 1989; Matyjaszewski et al., 1988). A recent reappraisal of the origins of the poly-modal molecular mass distributions, however, rationalizes this phenomenon in terms of a competition between polymer formation and degradation processes (Jones et al., 1996). Thus a satisfactory and unifying mechanistic theory as well as a general best procedure for the Wurtz reaction are still not available. To alleviate these drawbacks numerous modifications of the classic procedure were tested (Cragg et al., 1990; Miller and Jenker, 1994; Jones et al., 1995; Lacave-Goffin et al., 1995; Uhlig, 1995). For example, THF-soluble alkali metal complexes with 18-crown-6 have been used (Jedlinski et al., 1997). Here well-defined alkali-metal ion pairs ( $Mt^+/18\text{-crown-6}$ ,  $Mt^-$ ) are the reducing agents rather than



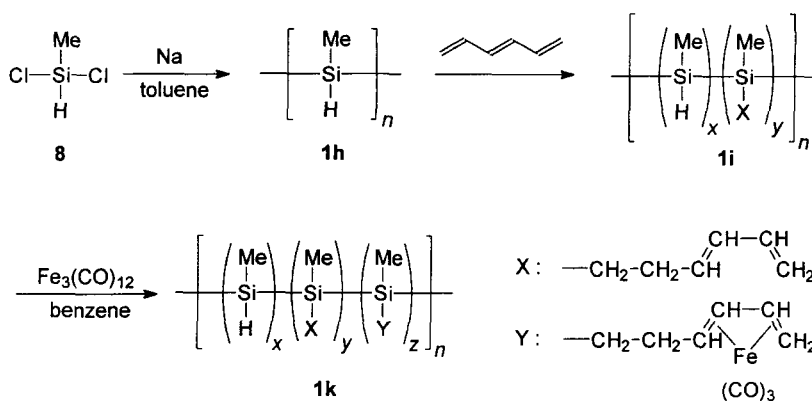
( $M_n > 8000$ ) has failed so far (Tilley, 1993). On the other hand, this route is important because it provides polysilanes with Si-H groups. Substitution of the hydrogen atoms (**1d**  $\rightarrow$  **1e**) allows the introduction of functional side groups into the polysilane backbone (Hsiao and Waymouth, 1994).

A second alternative to the Wurtz process is the ring-opening polymerization (ROP) of strained cyclosilane oligomers such as **6** under kinetic control (Cypryk et al., 1991; Fossum and Matyjaszewski, 1995). Moreover, Sakomoto et al. (1989) could show that polymerization of disilabicyclooctadienes like **7** – a masked disilene – leads to polysilanes such as **1g**. The polymerization most likely proceeds anionically, with elimination of the disilene fragment as a new silyl anion which can continue the reaction chain. Finally, some condensation reactions were tested to produce polysilanes: Polycondensation of  $\alpha,\omega$ -dilithiooligosilanes with dichlorosilanes (Wesson and Williams, 1980) and the thermal decomposition of silyl-mercury polymers (Maxka et al., 1991) may serve as examples.

Scattering data obtained from poly(di-*n*-hexylsilane) ( $M_w = 6\,000\,000$ ) indicate that polymers **1** form random coils in solution, but have a slightly higher chain stiffness than typical polyolefins (Cotts et al., 1987). The electronic and photochemical properties of polysilanes differ from those of all organic high polymers in that  $\sigma$ -electron delocalization is possible along the cumulated Si-Si bonds (Bock and Ensslin, 1971; Trefonas et al., 1983; Nelson and Pietro, 1988; Teramae and Takeda, 1989; Miller and Michl, 1989; Michl, 1990; Savin et al., 1992). Because the  $\sigma \rightarrow \sigma^*$  transition ( $\lambda_{\max} = 300 - 400$  nm) is permitted, the electronic absorptions are intense, with extinction coefficients  $\epsilon$  between 5000 and 10 000 per Si-Si bond (Trefonas et al., 1983; Takeda et al., 1986; Klingensmith et al., 1986).

Theoretical as well as experimental evidence indicates that  $\lambda_{\max}$  increases as the number of *trans* Si-Si-Si-Si conformations increases (Trefonas et al., 1983; Takeda et al., 1986; Michl et al., 1988; Miller et al., 1988). Therefore the  $\sigma$ - $\sigma^*$  separation depends on the conformation of the polysilane chains, and many polysilanes show reversible thermochromism (Lovinger et al., 1986; Miller and Michl, 1989; Weber et al., 1989; Schilling et al., 1990). Another consequence of  $\sigma$ -electron delocalization is the substantial electric conductivity of polysilanes after doping (Kepler et al., 1983, 1989): While the parent systems have conductivities of less than  $10^{-12}$  S cm $^{-1}$ , treatment with oxidizing agents like AsF $_5$  affords materials with conductivities of up to 0.5 S cm $^{-1}$  (West et al., 1981; Mark et al., 1992). Moreover, polysilanes are photoconducting (Kepler et al., 1982; Frey et al. 1994), can be used as charge transport materials in electrophotography (Stolka and Abkowitz, 1987; Stolka et al., 1987) or as transport layers in LEDs (Suzuki et al., 1993), and exhibit marked nonlinear optical properties (Baumert et al., 1988; Kajzar et al., 1986; Lovinger et al., 1989): The value of  $\chi^{(3)} = 11 \times 10^{-12}$  esu observed for poly(di-*n*-hexylsilane) is the largest ever observed for a polymer that is transparent in the visible region. Upon irradiation with ultraviolet light, most polysilanes undergo chain scission into smaller fragments (Trefonas et al., 1985; Karatsu et al., 1989). Thus polysilanes can be used as photoresists in microlithography (West, 1986; Miller and Michl, 1989; Mark et al., 1992).

Finally, they play an important role as precursors of silicon carbide ceramics (Miller et al., 1988). In this context, a novel synthetic route has been published recently which opens up access to Fe/Si/C composites as well: Iron tricarbonyl functionalized polysilanes **1k** (Scheme 10-3) were pre-



Scheme 10-3.

pared via hydrosilylation of conjugated trienes using **1h** followed by the treatment of **1i** with triiron dodecacarbonyl (Ungurenasu, 1996). First investigations concerning the thermal conversion of **1k** into ceramic materials have been reported to be promising.

### 10.3.2 Polygermanes and Polystannanes

In the 1980s, the first successful Wurtz synthesis of polygermanes,  $(\text{R}_2\text{Ge})_n$ , with  $M_n > 500\,000$  was published (Trefonas and West, 1985; Miller and Sooriyakumaran, 1987; Miller and Michl, 1989). Later on, Mochida and Chiba (1994) developed an alternative route to polygermanes using diiodogermylene,  $\text{GeI}_2$ , and alkyl Grignard reagents or organolithiums. This latter method is experimentally easier and safer than the Wurtz process and gives higher yields of narrowly distributed but relatively low molecular weight polygermanes ( $M_w \approx 10^3 - 10^4$ ). After further optimization, the titanocene- or zirconocene-catalyzed dehydrogenative coupling of germanium hydrides might also develop into an efficient synthetic route to polygermanes (Harrod, 1988).

The chain structure and material properties of polygermanes are similar to those of

polysilanes **1** (Aitken et al., 1988; Miller and Michl, 1989; Hallmark et al., 1990; Welsh and Johnson, 1990): Polygermanes decompose and volatilize upon exposure to radiation (Mochida and Chiba, 1994) and thus might be useful in microlithography (Miller and Michl, 1989; Hallmark et al., 1990).  $\sigma$ -Electron delocalization is more pronounced than in **1** and thus  $\lambda_{\text{max}}$  is shifted bathochromically by about 20 nm in high molecular weight polygermanes (Trefonas and West, 1985; Miller and Sooriyakumaran, 1987). An even more pronounced  $\sigma$ -electron delocalization was expected for polystannanes,  $(\text{R}_2\text{Sn})_n$  (Adams and Dräger, 1987; Takeda and Shiraishi, 1992; Sita et al., 1995). However, until 1992 the longest known stannane chain had only nine metal centers (Devlyder et al., 1996; Brown and Morgan, 1963; Neumann and Pedain, 1964; Mitchell, 1975; Grugel et al., 1977; Adams and Dräger, 1987). Zou and Yang (1992) were the first to prepare really high molecular weight linear polystannanes via 15-crown-5-catalyzed Wurtz coupling of  $\text{Bu}_2\text{SnCl}_2$ . Subsequently, Imori and co-workers (Imori and Tilley, 1993; Imori et al., 1995) obtained similar polymers through zirconium-catalyzed dehydrogenation of secondary stannanes. Finally, an improved Wurtz synthesis has been described by Devlyder

et al. (1996) which yields poly(dibutylstannanes) of very high molecular weights ( $M_n \approx 10^6$ ; GPC). In this study, the reaction time was identified as the key parameter, since polymers degrade upon prolonged reaction. A detailed investigation of the polystannanes thus available ( $M_w \approx 96\,000$ ,  $M_n \approx 22\,000$ ) showed a highly extended  $\sigma$ -delocalization in these polymers ( $\lambda_{\max} = 384\text{--}388\text{ nm}$ ; THF). Upon doping with  $\text{AsF}_5$ , an electrical conductivity of up to  $0.3\text{ S cm}^{-1}$  was determined (Imori et al., 1995).

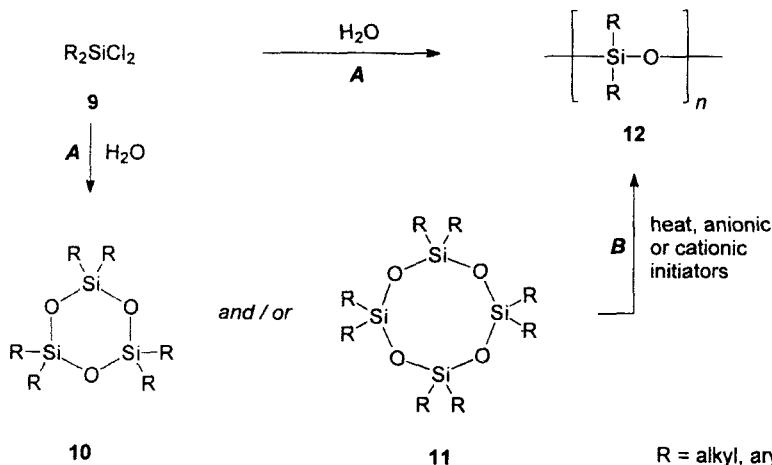
### 10.3.3 Polysiloxanes

Polysiloxanes represent by far the most studied and economically most important hybrid polymers worldwide (Archer, 1986; Zeldin, 1986; Rheingold, 1987; Rochow, 1987; Patai and Rappoport, 1989; Bock, 1989; Goodwin and Kenney, 1990; Zeigler and Fearon, 1990; Allcock and Lampe, 1990; Semlyen and Clarson, 1991; Sheats et al., 1991; Clarson and Semlyen, 1991; Mark et al., 1992; Manners, 1996). They can be produced via polycondensations, or via anionic or cationic ROP reactions.

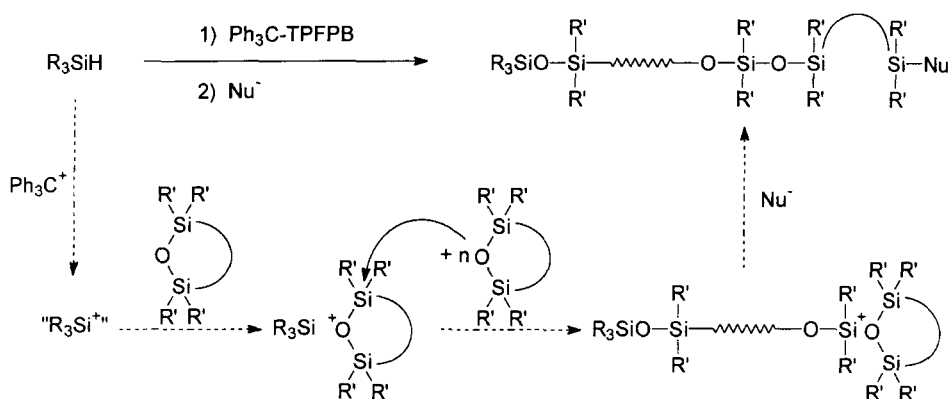
In the polycondensation approach (Scheme 10-4 A), dichlorodialkylsilanes **9**

are hydrolyzed to give long chain linear (**12**) and/or cyclic siloxanes such as **10** and **11** via hydroxy intermediates. Basic catalysts and high temperatures favor linear, high molecular weight polymers, while acidic catalysts tend to produce cyclic and/or linear oligomers (O dian, 1991). Today, this “hydrolysis approach” has been largely replaced by the ROP of organosilicon cyclic trimers and tetramers **10** and **11**, respectively (Scheme 10-4 B) (Rochow, 1987; Kendrick et al., 1989; McGrath, 1985; Saam, 1990; Chojnowski, 1991 a). Typical catalysts for the anionic ROP are alkali metal oxides, hydroxides, and bases in general. The controlled polymerization of hexa-*n*-alkylcyclotrisiloxanes using cryptated lithium, moreover, yields polymers with low polydispersity, demonstrating the presence of a single growing species in this case (Moltenberg et al., 1997). Finally, the “living” anionic ROP of cyclic siloxanes opens up elegant access to block copolymers (Chojnowski, 1991 b; Stein et al., 1991).

Cationic ROP of cyclosiloxanes, on the other hand, has not received as much attention as the anionic variety. Despite the fact that the results are generally similar to those of the anionic ROP, the mechanism is very different (Wilczek et al. 1986; Kendrick



Scheme 10-4.



Scheme 10-5.

et al., 1989). It is assumed that two active ends per chain are involved in the propagation process, and both condensation and addition polymerization must be considered here. However, Wang et al. (1996) recently described a modified cationic ROP of cyclosiloxanes which was initiated by electrophilic organosilicon reagents such as  $R_3SiH-Ph_3C^+B(C_6F_5)_4^-$  ( $Ph_3C-TPFPB$ ) in the absence of protic acids. This latter ROP is of substantial interest from the mechanistic and synthetic point of view, as in this case the chains propagate at only one single “long-lived” oxonium ion end. The proposed mechanism is outlined in Scheme 10-5.

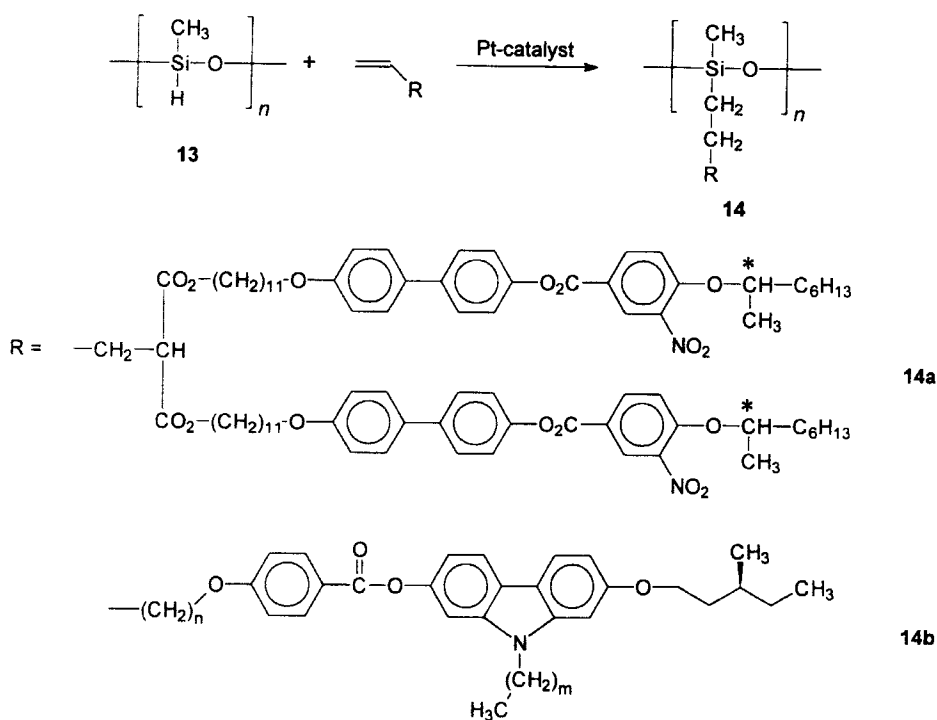
A versatile method for subsequent modification of the substitution pattern of polysiloxanes is hydrosilylation. The reaction of poly(methylhydrosiloxane) **13** (Scheme 10-6) with vinyl compounds, for example, allows the introduction of side chains and thus opens up access to an enormous variety of products (Boileau and Teysie, 1991), such as the ferroelectric liquid-crystalline polysiloxane **14a** (Poths and Zentel, 1994) or carbazole-containing polymers like **14b**, some of which show smectic thermotropic mesophases (Arnim et al., 1996).

A modified hydrosilylation strategy was used by Hempenius et al. (1996 a, b, 1997),

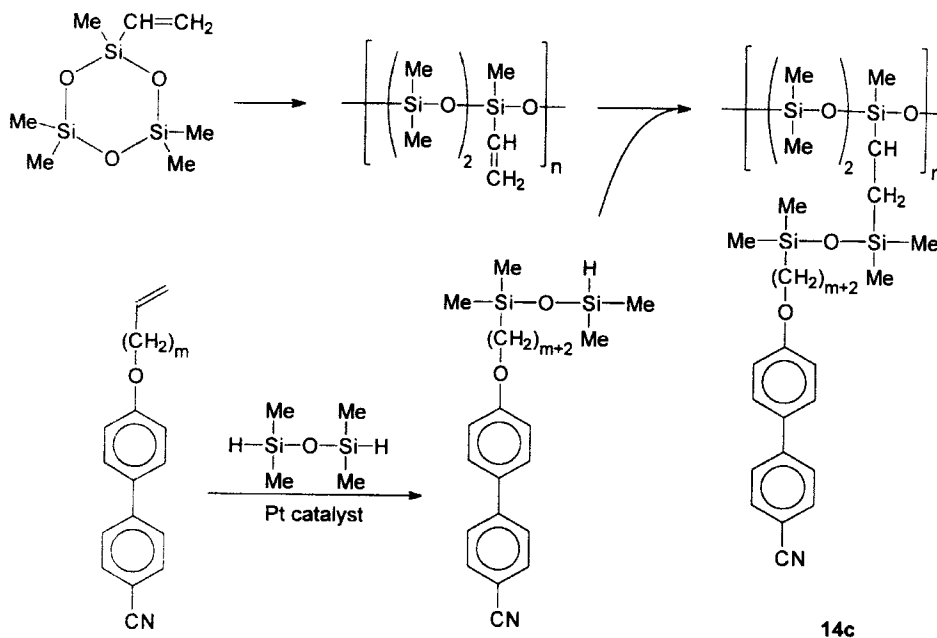
who report on liquid-crystalline polysiloxanes **14c** (Scheme 10-7) ( $M_w \approx 10\,000$ ;  $M_w/M_n < 1.2$ ; GPC) whose electro-optic switching times are  $\tau_s = 1$  min at  $20^\circ C$  and  $7$  s at  $32^\circ C$ . Very recently, the controlled synthesis of siloxane copolymers **14d** (Scheme 10-8) having organosulfur groups has been reported (Róžga-Wijas et al., 1996). Here, a cryptand-lithium silanolate complex was selected as the initiator for the ROP synthesis, and the sulfur groups were generated by the ene-thiol addition to the vinyl functions bound to silicon. Both synthetic routes (shown in Scheme 10-8) give high yields of copolymers **14d** of fairly regular chain structure.

Another development is the preparation of poly(dimethylsiloxanes), randomly substituted with up to 37% calix[4]arene or benzo-15-crown-5 moieties (Klok et al., 1997), or with polar cyanopropyl and crosslinkable methacryloxypropyl groups. The latter polymers have superior diffusion and permeability coefficients and might be useful as matrices for  $Na^+$ -sensitive membranes in chemically modified field effect transistors (Gankema et al., 1994). Polysiloxanes **14e** bearing  $Ru(bpy)_3^{2+}$  pendant groups have been reported by Nagai et al. (1996). The emission of films of **14e** was quenched by oxygen in water more efficiently than in





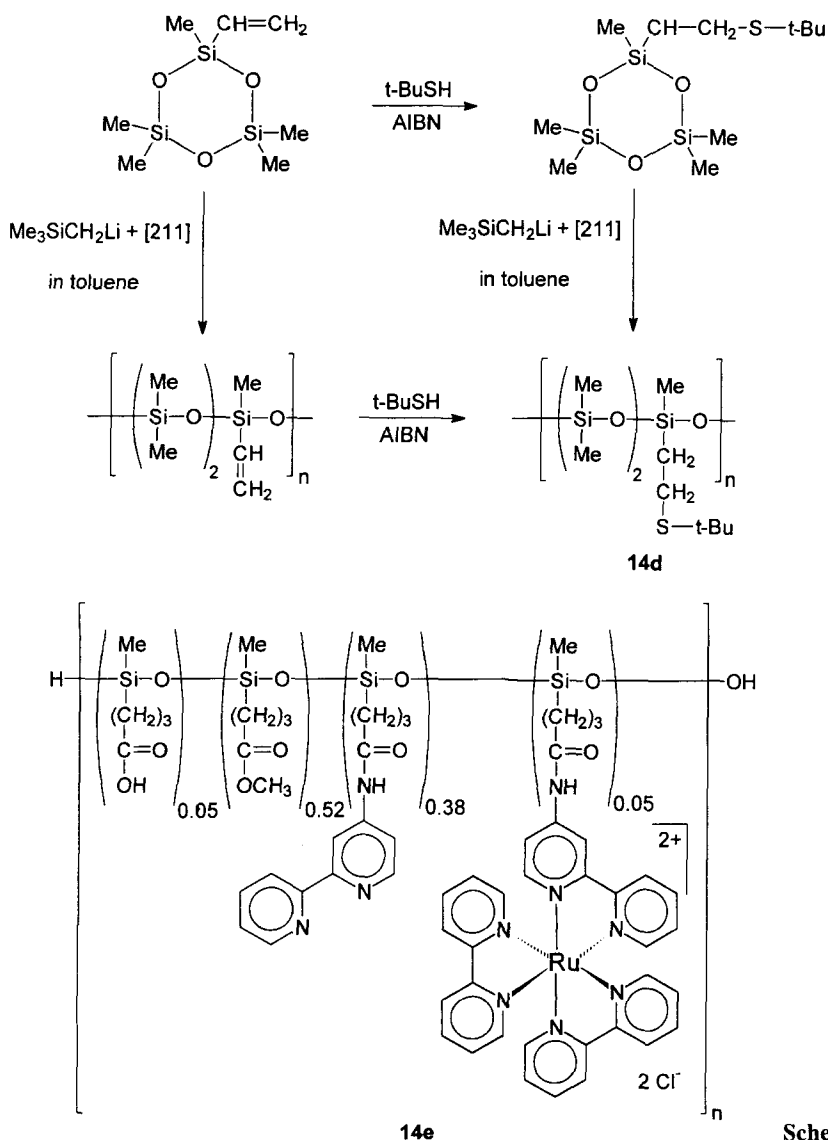
Scheme 10-6.



Scheme 10-7.

the gas phase. From this result, the authors conclude that polysiloxane chains have a specific affinity for oxygen molecules in water. In addition to this, the siloxane back-

bone is one of the most flexible of all known polymers (Flory, 1969; Oberhammer and Boggs, 1980; Lukevics et al., 1989; Mark, 1990). Even at very low temperatures, these



materials maintain their elasticity: poly(dimethylsiloxane) for example has a  $T_g$  of  $-123^\circ\text{C}$ , and poly(methylhydrosilane) has a still lower glass transition temperature ( $T_g = -137^\circ\text{C}$ ).

Another important property of polysiloxanes is their exceptional stability against heat, oxidation, and UV radiation. Depending on the side chains, moreover, polysiloxanes may have very low surface free ener-

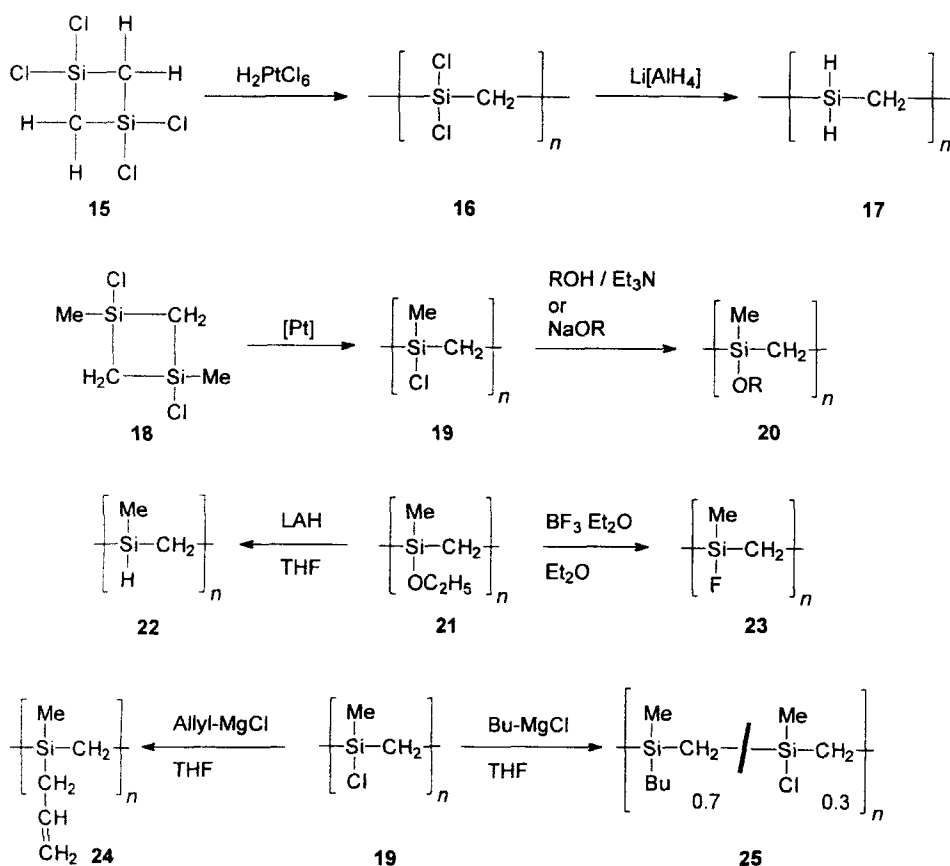
gies and are therefore widely used as coatings, mold-release agents, surface modifiers, or separation membranes. Finally, their chemical inertness and high gas permeability make them attractive in biomedicine where they are used for soft contact lenses, artificial skin, body implants, or controlled-release systems (Arkles, 1983; Rochow, 1987; Semlyen and Clarson, 1991; Mark et al., 1992).

### 10.3.4 Polycarbosilanes

The first polycarbosilanes were reported in the 1960s, but intensive polycarbosilane research started about ten years ago (Weyenberg and Nelson, 1965; Cundy and Lapert, 1978; Yamashita et al., 1995). A milestone in polycarbosilane research was the synthesis of poly(silylene methylene) **17** (Scheme 10-9), i.e., polysilaethylene, as recently published by Interrante et al., which involves the platinum-catalyzed ROP of **15**, leading to poly(dichlorosilaethylene) **16**, followed by reduction using LAH (Wu and Interrante, 1992; Interrante et al., 1994; Rushkin and Interrante, 1995). Using the

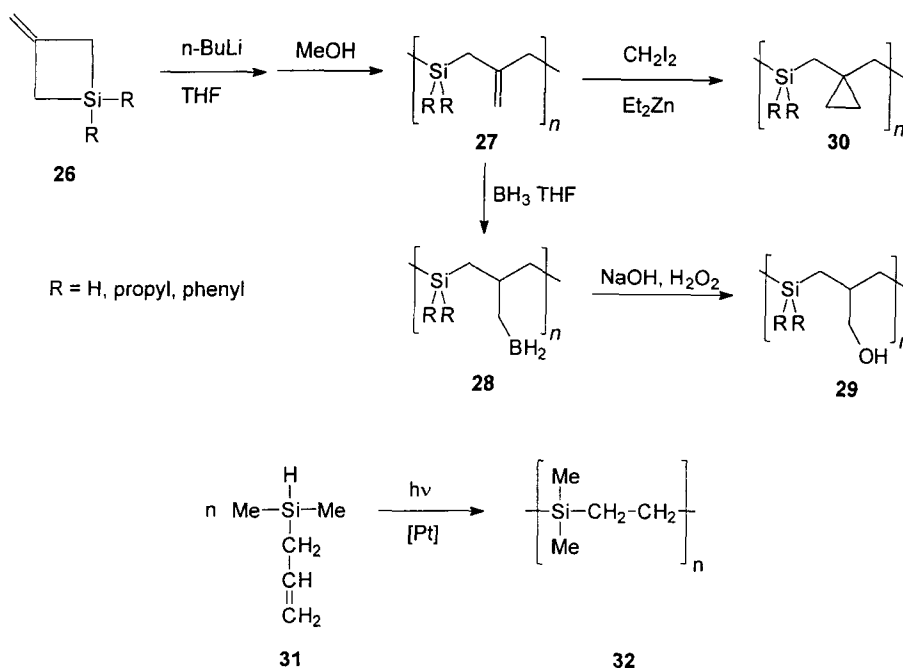
thus-developed route, a variety of further poly(silylene methylene) derivatives have been prepared, such as **19–26** (Shen and Interrante, 1996; Rushkin and Interrante, 1996 a). Also, some  $[\text{Si}(\text{Me})(\text{C}_3\text{H}_6\text{R})\text{CH}_2]_n$  polymers were obtained by hydrosilylation, having  $\text{R}=\text{C}_3\text{H}_7$ ,  $\text{NEt}_2$ , carbazole, and  $\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OCH}_3$  (Rushkin and Interrante, 1996 b).

While polymer **17** ( $T_m \approx 25^\circ\text{C}$ ,  $T_g \approx -135$  to  $-140^\circ\text{C}$ ) is stable in air and dissolves readily in common organic solvents, the hydrolytic sensitivity and glass transition temperature of polymers **20** were found to vary widely depending on their  $\text{R}$  groups. Koopmann and Frey (1996) report poly(silylene



Scheme 10-9.

$\text{R} = \text{Et}, \text{OCH}_2\text{CF}_3, \text{C}(\text{O})\text{CH}_3, \text{C}_6\text{H}_5$

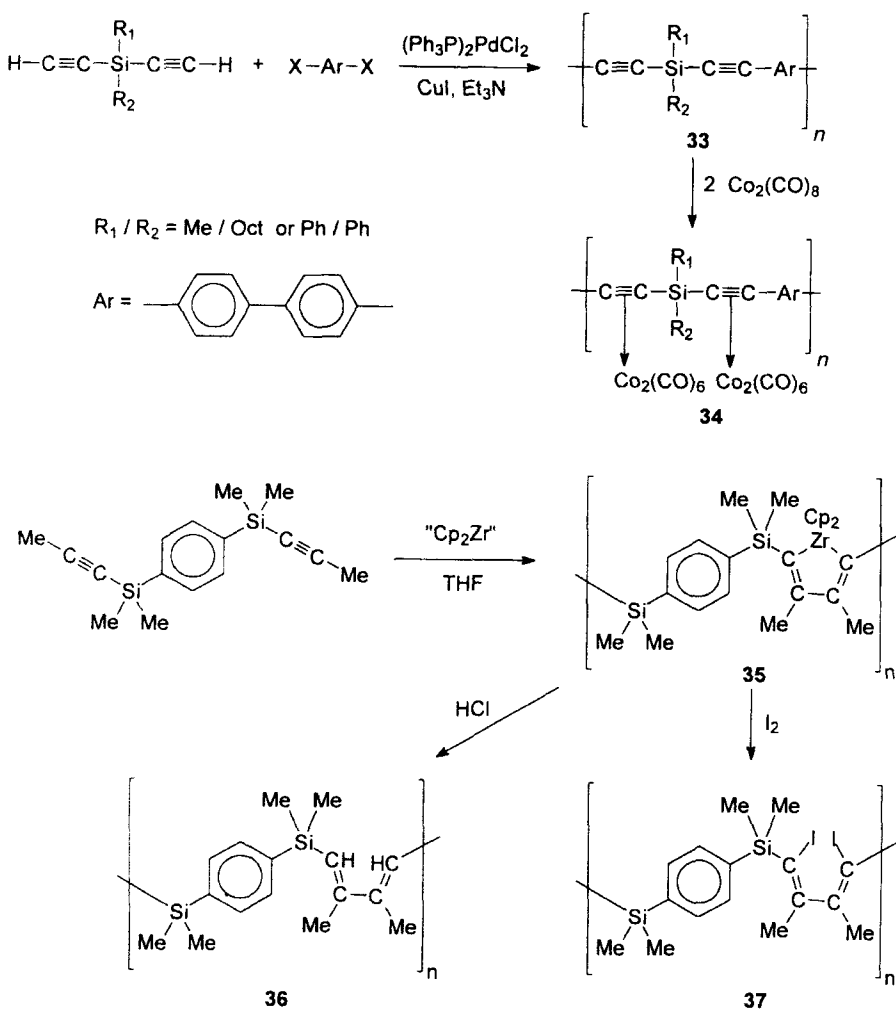


Scheme 10-10.

methylenes) with long *n*-alkyl side chains which have been prepared via cationic ROP of tetraalkyl-substituted 1,3-disilacyclobutanes. Longer polymerization times were found to be necessary in comparison to the case for monomers with methyl groups only, and the backbone flexibility of these poly(silylene methylenes) proved to be lower than that of the analogous poly(di-*n*-alkylsiloxanes). Unusual polycarbosilanes have been described by Matsumoto et al. (1997): Anionically initiated ROP of 3-methylene-silacyclobutanes **26** (Scheme 10-10) gave polymers **27** ( $M_n=28\,000$ ,  $M_w/M_n=1.8-2.9$ ; GPC) which were subsequently subjected to (i) hydroboration followed by oxidative work-up or (ii) cyclopropanation, leading to polymers **29** and **30**, respectively. The hydroboration occurs without side reactions, while a somewhat less homogeneous conversion was found for the cyclopropanation reaction. A photoactivated platinum-catalyzed hydrosilylation polymerization of vinyltrimethylsilane **31** has

been found by Fry and Neckers (1996). Once photoactivated, the catalyst remains active for an indefinite period of time, and the poly(dimethylvinylsilane) oligomers **32** formed shortly after irradiation ( $M_w=5500$ ) grow further up to  $M_w=12\,300$  after six months due to end-linking of their hydride and vinyl termini.

A variety of polycarbosilanes is known whose main chains contain unsaturated hydrocarbon moieties (West et al., 1991; Wagener and Smith, 1991; Anhaus et al., 1991; Corriu et al., 1992; Bréford et al., 1992; Ishikawa et al., 1992; Sargeant et al., 1992; Theurig et al., 1992): Poly(silylene ethynylene-*alt*-phenylene ethynylenes) were prepared for example by dehydrogenative polymerizations using MgO as a catalyst, or by condensation reactions using Grignard intermediates. Silicon analogs of poly(*p*-phenylenevinylene) were also synthesized using the Wittig reaction (Kim et al., 1997). The photoluminescence of the polymers thus obtained ( $M_n=2500-2800$ ; GPC) ap-

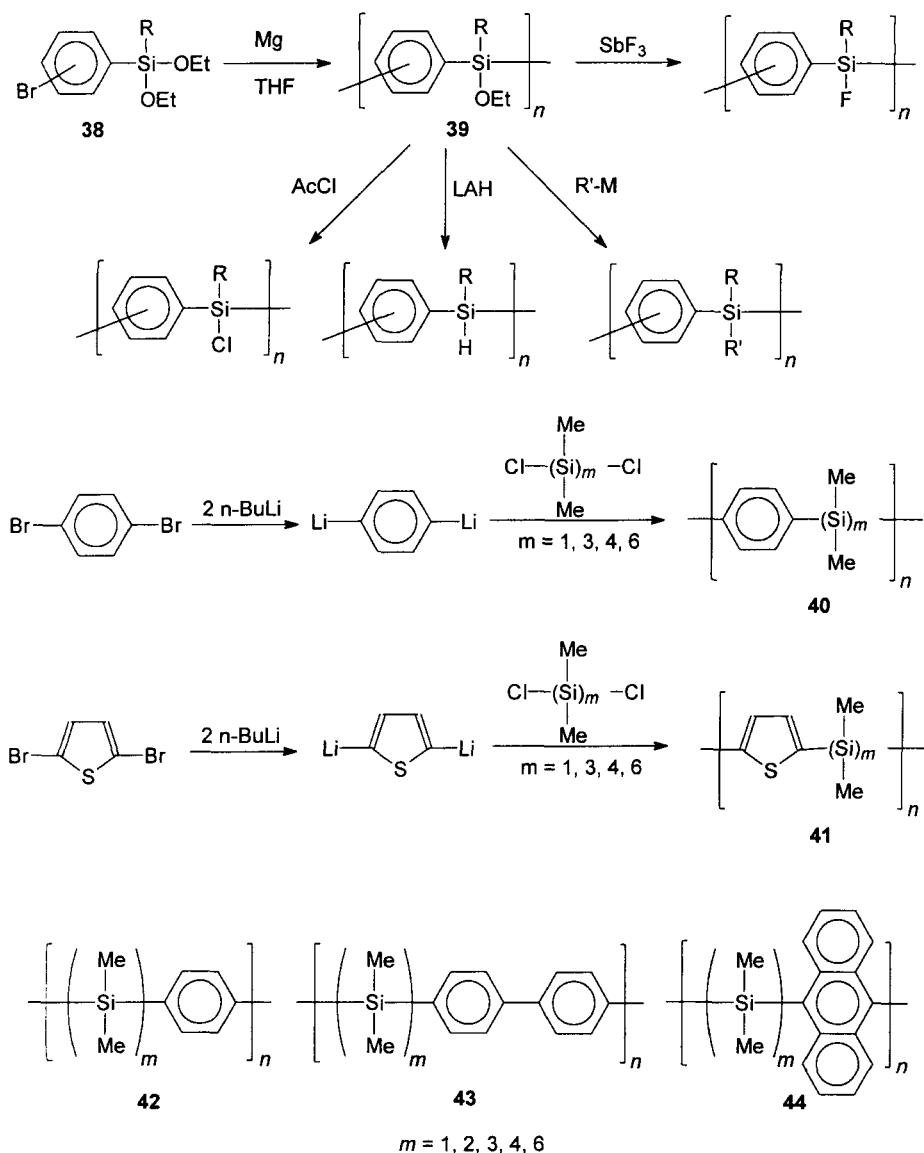


Scheme 10-11.

appears at around  $\lambda_{\text{max}} = 440\text{--}480\text{ nm}$  in the blue emission region, and makes these polymers attractive for LED applications. Cobalt-containing polycarbosilanes **34** (Scheme 10-11) were prepared by Corriu et al. (1993) from precursor polymers **33** [which are semiconducting after doping (Corriu et al., 1991) and have a high and stable nonlinear optical  $\chi^{(2)}$  value if Ar is a donor-acceptor group (Cross et al., 1992)] by reaction with dicobalt octacarbonyl. Mao and Tilley (1995) describe a simple procedure for the incorporation of zirconacyclopentadienyl rings into polymers such as **35**

which have been shown to be versatile and efficient precursors to, on the one hand, polymers such as **36** and **37**. On the other hand, **35** degrades upon heating, leading to the cyclic trimer.

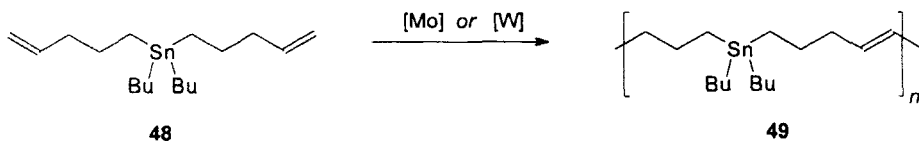
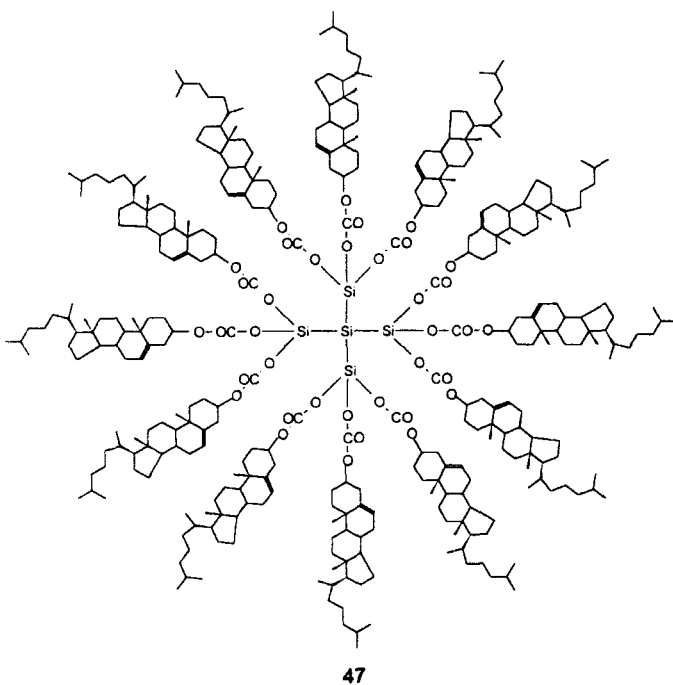
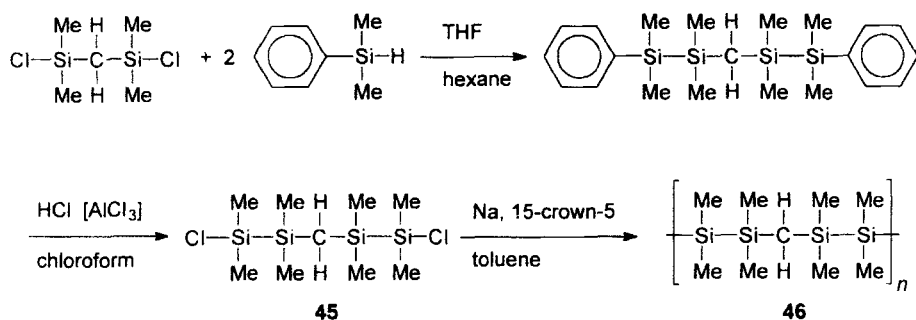
Ohshita et al. (1997) published the synthesis of poly[(ethoxysilylene)phenylenes] **39** (Scheme 10-12) by the treatment of **38** with magnesium metal. The OEt groups of the soluble polymers **39** ( $M_w = 10\,000\text{--}30\,000$ ;  $M_w/M_n = 1.6\text{--}1.8$ ) could be replaced by many other substituents including H, F, Cl, or another substituent  $R'$ .



Scheme 10-12.

In 1995, Fang et al. described soluble silylene-phenylene and silylene-thienylene copolymers **40** and **41**, respectively ( $M_w = 2500 - 7500$ ). An enhancement of  $\sigma$ - $\pi$  conjugation between the dimethylsilylene units and the  $\pi$ -conjugated units with increasing dimethylsilylene chain length was suggested. Later on, another series of  $\sigma$ - $\pi$  conjugated organosilicon copolymers

**42–44** was described consisting of alternating dimethylsilylene and aromatic units. Here as well, the emission decay and the quantum yield suggest  $\sigma$ - $\pi$  conjugation along the organosilicon copolymer chains (Fang et al., 1996). In 1997, Isaka reported the  $\text{Si}_4\text{C}$ -type periodic polycarbosilane **46** (Scheme 10-13) which was prepared via Wurtz coupling of **45**. Its  $\sigma$ - $\sigma^*$  transition en-



Scheme 10-13.

ergy is shown to vary from 5.2 to 4.5 eV. Strong Stokes shifts (1.2 eV) indicate that the emission is due to a “self-trapped” exciton state.

Some carbosilane dendrimers have been reported as well (van der Made and van Leeuwen, 1992; Zhou and Roovers, 1993;

Coen et al., 1996; Lach et al., 1997), such as the mesogen-functionalized G1 dendrimer **47** bearing 12 cholesteryl end groups. The corresponding G2 and G3 systems bearing 36 and 108 mesogenic groups, respectively, are also described (Coen et al., 1996). Finally, some papers deal with the germani-

um- and tin-analogs of polycarbosilanes. In general, the same synthetic methods can be used for their preparation [see, for example, Corriu et al. (1990), Bréfort et al. (1992, 1994)]. In addition to this, Wolfe et al. (1997) reported an elegant acyclic diene metathesis leading to well-defined polycarbostannanes **49**, utilizing both a well-defined molybdenum alkylidene and an aryloxo tungsten “classic” catalyst system. In both cases, the polymerization proceeded smoothly to produce linear polymers **49** which were characterized using proton, carbon, and tin NMR. Molecular weights of about 16 000 can be reached.

### 10.3.5 Polyphosphazenes

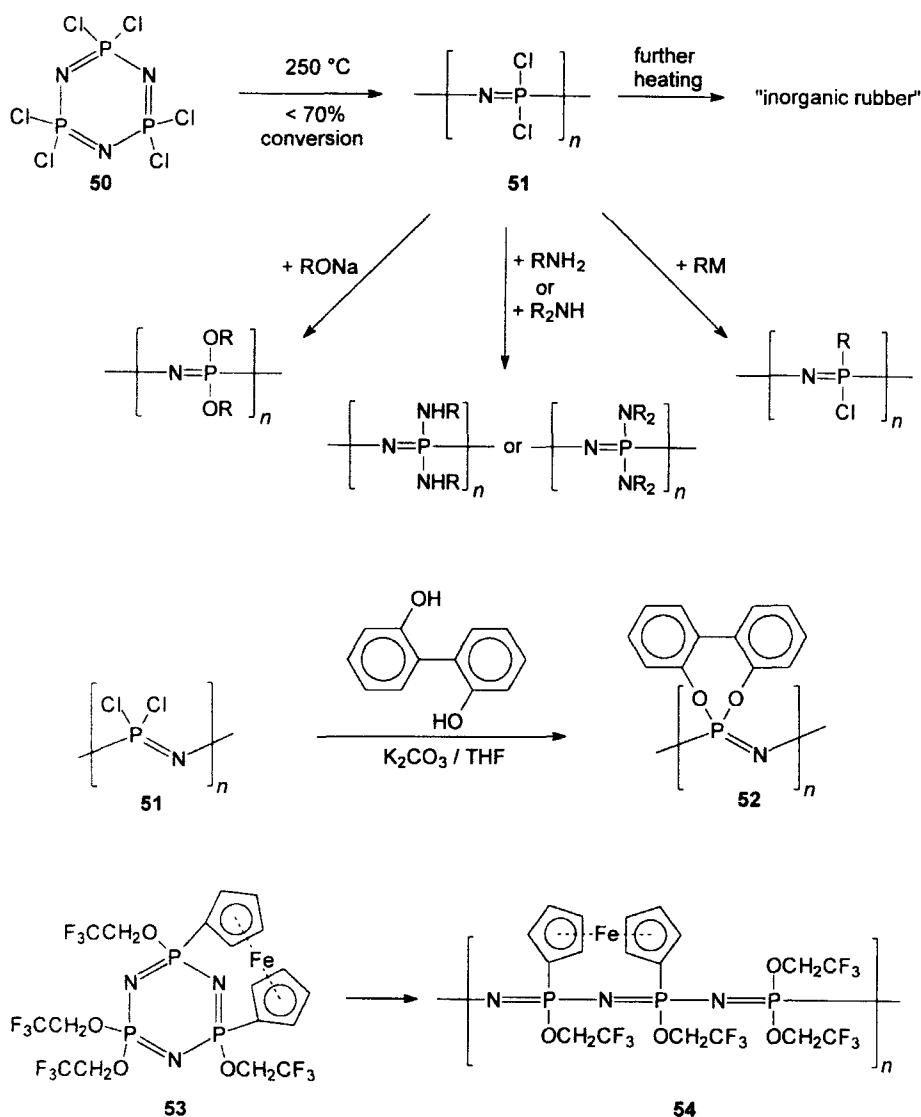
Polyphosphazenes, by far the largest class of hybrid polymers known today, have a backbone that consists of alternating phosphorus and nitrogen atoms with two side groups, *R*, being attached to each phosphorus (Mark et al., 1992). *R* may be organic, organometallic, or inorganic. Stokes (1895–1898) was the first to suggest that the reaction of  $\text{PCl}_5$  and  $\text{NH}_3$  leads to a mixture of cyclic products  $(\text{NPCl}_2)_{x < 8}$  which transform into a crosslinked elastomeric material known today as “inorganic rubber” when heated. This material, however, remained a curiosity for a long time because it was insoluble, unprocessable, and very unstable against water. This situation persisted until the mid-1960s when Allcock et al. (Allcock and Kugel, 1965, 1966; Allcock et al., 1966; Neilson and Wisian-Neilson, 1988) showed that unbranched, soluble polymers **51** (Scheme 10-14) are available when the thermal ROP of **50** is carried out with careful control of the reaction conditions. Moreover, they took advantage of the high reactivity of the P-Cl bonds to transform the hydrolytically unstable polymers

**51** into hydrolytically more stable derivatives: Treatment of **51** with organic nucleophiles such as the sodium salts of alcohols or phenols, or with primary or secondary amines, brought about total replacement of the chlorine atoms by the organic units (Allcock and Mack, 1970; Allcock and Chu, 1979; Allcock et al., 1977; Allcock, 1992, 1994 a, b).

Still today, this macromolecular substitution route is used as the standard synthetic route for many polyphosphazene derivatives, and is perhaps the most important feature of polyphosphazene chemistry as it allows variation of the side groups *R* over a very wide range. Recent publications dealing with the derivatization of **51** and related compounds describe the introduction of side groups *R* which result in liquid crystallinity (Allcock and Kim, 1989), photochromism (Allcock and Kim, 1991), photocrosslinkability (Allcock et al., 1991a; Facchin et al., 1991; Allcock and Cameron, 1994), and short chain branches (Ngo et al., 1991; Allcock et al., 1994 a). A new type of phosphazene high polymer containing 2,2'-dioxybiphenyl groups was reported by Carriedo et al. (1996), who showed that the direct reaction of **51** ( $M_w \approx 1\,000\,000$ ) with the difunctional reagent 2,2'-dihydroxybiphenyl and  $\text{K}_2\text{CO}_3$  in THF gives soluble, linear polyphosphazenes **52** instead of the expected crosslinked products.

Yet the macromolecular substitution route also has limitations if the target polymers are to contain essentially organic side groups linked to the skeleton through carbon-phosphorus bonds. Unlike their oxo- or nitrogen-nucleophile counterparts, organometallic reagents generate more complicated reactions (Allcock et al., 1977; Allcock and Chu, 1979). For example, the interaction of **51** with  $\text{RMgX}$  or  $\text{RLi}$  usually follows two competitive and conflicting pathways. Replacement of chlorine by the group

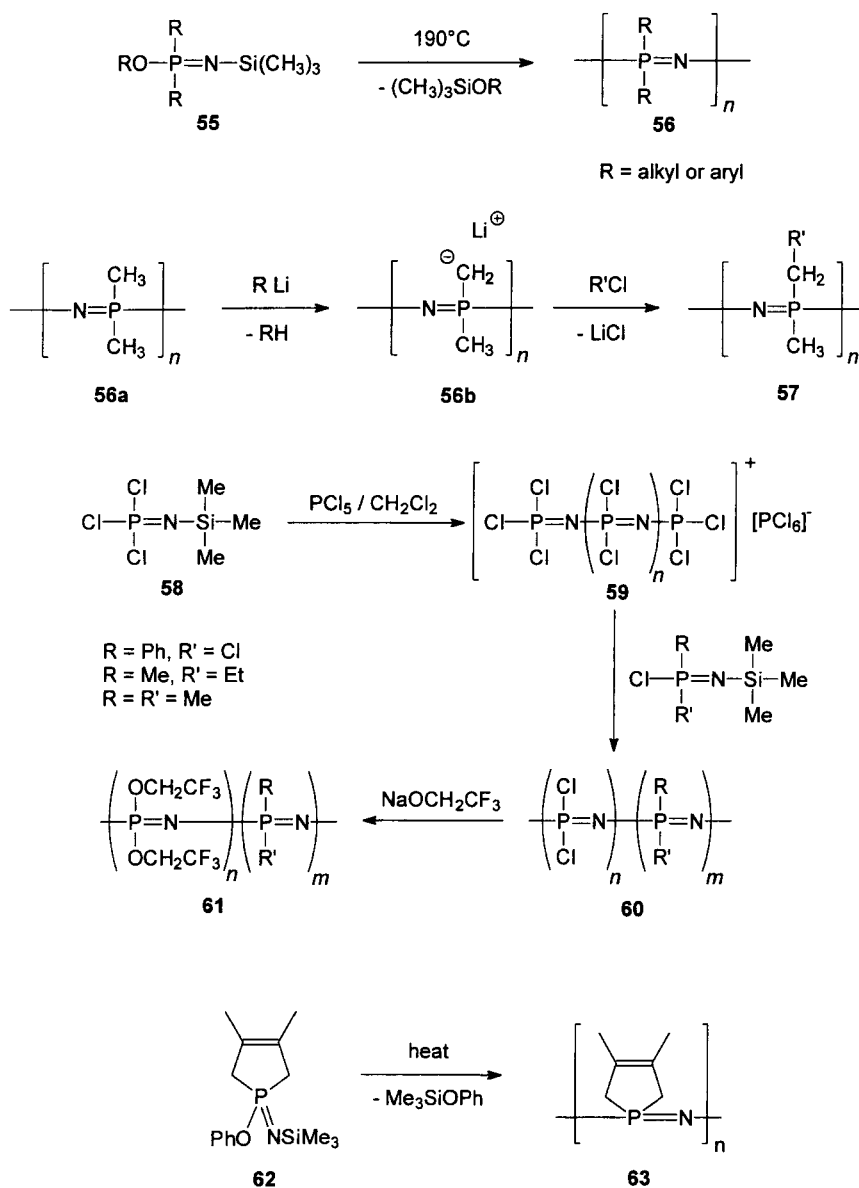




Scheme 10-14.

*R* certainly occurs, but this is accompanied by (or followed by) cleavage of the phosphorus-nitrogen bonds in the skeleton. Thus special techniques are required to replace chlorine (or fluorine) side units without significant skeletal cleavage (Allcock et al., 1987). Two alternative approaches were developed which completely avoid the interaction of organometallic reagents with high polymeric phosphazenes. The first one involves the introduction of the organic (or or-

ganometallic) side groups at the cyclic trimer level, followed by ring-opening polymerization (Prons et al., 1971; Ritchie et al., 1979; Allcock, 1980; Scopelianos et al., 1980; Allcock et al., 1985; Allcock and Brennan, 1988). However, while cyclic trimers with only one or two organic or organometallic side groups usually polymerize almost as easily as  $(NPCl_2)_3$  or  $(NPF_2)_3$ , the tendency towards polymerization declines as more and more halogen atoms in the



Scheme 10-15.

trimer are replaced by organic groups (Allcock and Moore, 1975). This restriction does not exist if the phosphazene ring is strained by, for example, the presence of a transannular ferrocenyl group like in **53** (Manners et al., 1989a). Here, polymerization takes place to give polymer **54** even if no halogen atoms are attached to the phosphorus atoms.

The second way to prepare polyorgano-phosphazenes is condensation reactions such as **55** → **56** (Scheme 10-15) (Wisian-Neilson, 1980; Neilson et al., 1987; Neilson and Wisian-Neilson, 1988). Although this approach is somewhat restricted, in the sense that the variety of side groups that can be incorporated is limited, the polymers obtained by this route are exactly those that are

so difficult to produce by the macromolecular substitution approach. Moreover, polymers such as **56a** undergo lithium-hydrogen exchange reactions to give anionic species **56b**, and these react with organic or organometallic halides to give further derivatives such as **57** (Wisian-Neilson et al., 1986). Very recently, Allcock et al. (1996) reported the "living" cationic polymerization of phosphoranimines as an ambient temperature route to polyphosphazenes with controlled molecular weights. This new method involves the initiation of  $\text{Cl}_3\text{P}=\text{NSiMe}_3$  (**58**) with small amounts of  $\text{PCl}_5$  in  $\text{CH}_2\text{Cl}_2$  to yield poly(dichlorophosphazenes) with narrow polydispersities.  $\text{PBr}_5$ ,  $\text{SbCl}_5$ , and  $\text{Ph}_3\text{C}^+[\text{PF}_6]^-$  were also found to be effective initiators in  $\text{CH}_2\text{Cl}_2$  at room temperature. Moreover, the polymer chains **59** were found to be active after chain propagation. Thus this method allows the synthesis of block copolymers like **60** and **61** (Montague and Matyjaszewski, 1990; Matyjaszewski, 1992; Matyjaszewski et al., 1992, 1994; Allcock et al., 1997).

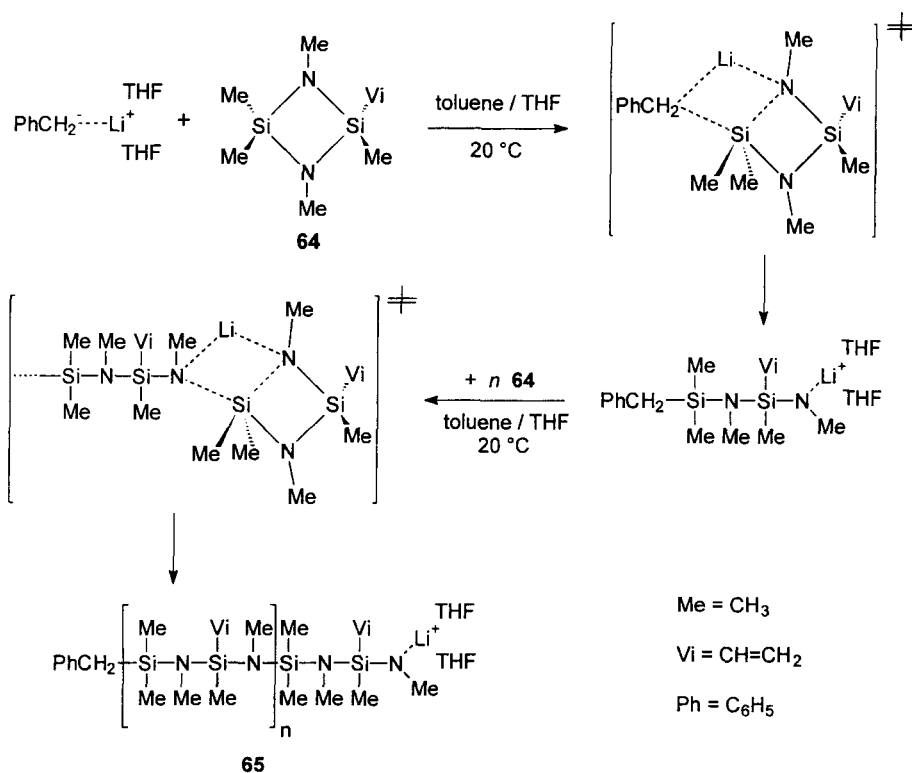
The synthesis of a new phosphazene polymer, i.e., poly(phospholenazene) **63** ( $M_w \approx 40\,000 - 50\,000$ ,  $M_w/M_n \approx 3.3$ , GPC) has been reported recently by Gruneich and Wisian-Neilson (1996). It was found that only small amounts of the 3,4-isomer **62** were converted to the 2,3 isomer during thermolysis. After extensive handling in air, however, the solubility of **63** decreases, presumably due to reactions at the unsaturated sites in the ring. In addition to the polymers shown, many other polyphosphazenes exist which may serve as solid electrolyte materials, for optical applications, or as gas permeation membranes (Mark et al., 1992; Manners, 1996). Moreover, many polyphosphazenes are of interest since they have an enormous chain flexibility and thus very low glass transition temperatures:  $(\text{NPCl}_2)_n$ , for example, has a  $T_g$  of  $-66^\circ\text{C}$ , and the  $T_g$

of  $[\text{NP}(\text{OC}_3\text{H}_7)_2]_n$  is  $-100^\circ\text{C}$ . Also, polyphosphazenes are distinguished by a high thermal and oxidation stability, optical transparency from 220 nm up to near IR, and high stability towards hydrocarbons.

The bond structure in the polyphosphazene backbone is formally represented as a series of alternating single and double bonds. However, this formulation is misleading as all the bonds along the chain are equal or nearly equal in length, but without an extensive conjugation. It is believed that the electron on nitrogen is accommodated in a  $2p_z$  orbital while the one from phosphorus is in a  $3d$  orbital (Dewar et al., 1960). Thus, although the  $\pi$ -bonds are delocalized over three atoms ("island"  $\pi$ -bond structure), they are not broadly delocalized over the whole chain because of the orbital mismatch and nodes that occur at every phosphorus. This may explain why most polyphosphazenes are colorless materials. On the other hand, because each phosphorus atom can use as many as five  $3d$  orbitals, torsion of a P-N bond brings the nitrogen  $p$  orbital into an overlapping position with a phosphorus  $d$  orbital at virtually any torsion angle. Hence the inherent torsional barrier is much smaller than in a  $p_\pi$ - $p_\pi$  double bond of the type found in organic molecules.

### 10.3.6 Polysilazanes

Up to recently, the ROP synthesis of high molecular weight linear polysilazanes failed due to termination, transfer, and ring-condensation side reactions (Andrianov et al., 1965; Blum and Laine, 1986; Seyferth et al., 1989; Bruzard and Soum, 1996). However, this reaction was reinvestigated recently, and it was established that high molecular weight linear polymers are available via both anionic and cationic ROP of specific cyclodisilazanes (Duguet et al.,



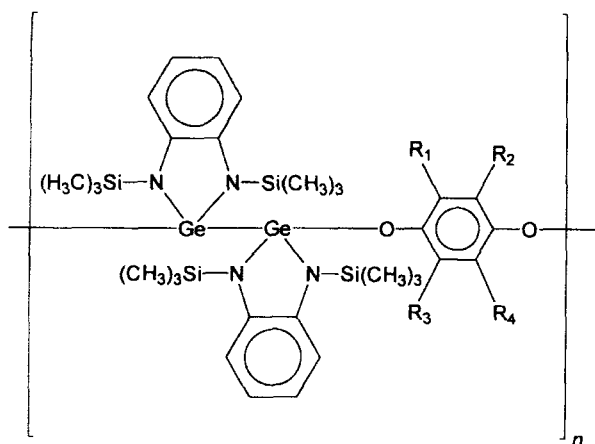
Scheme 10-16.

1992). Moreover, when optimized conditions are adhered to, the anionic ROP initiated with organosodium and organolithium initiators exhibits all the characteristics of a living process. On the basis of kinetic measurements, a mechanism of the anionic ROP is proposed, which is shown in Scheme 10-16 (Bruzaud and Soum, 1996; Bruzaud et al., 1997).

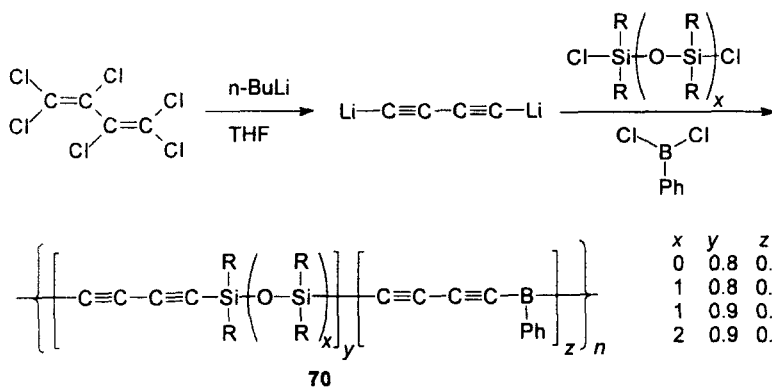
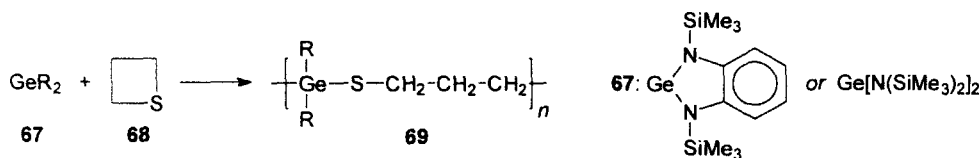
In another recent paper, the solid state structure and transition properties of three poly(*N*-methylsilazanes) are described (Tang et al., 1997). These results will stimulate for sure further research activities on polysilazanes which are of particular interest as precursors to ceramics or fibers usable at very high temperatures (Laine et al., 1988; Soula, 1988; Duguet et al., 1992; Bouquey et al., 1996; Bruzaud and Soum, 1996).

### 10.3.7 Further Main Group Hybrid Polymers

In recent years, novel synthetic methods such as the ROP technique have opened up access to many further hybrid polymers with main group elements in their backbone, like polyoxothiazenes (Seel and Simon, 1960; Parshall et al., 1962; Roy, 1992; Roy et al., 1993), polycarbophosphazenes (Manners et al., 1989 b; Allcock et al., 1991 b; Allcock et al., 1993 a; Allcock et al., 1994 b), and sulfur-nitrogen-phosphorus polymers (van de Grampel, 1981; Dodge et al., 1990; Liang and Manners, 1991 a, b; Allcock et al., 1993 b; Ni et al., 1996 a). An interesting system is the recently reported copolymer **66** (Scheme 10-17), which is available via copolymerization of cyclic germylenes and *p*-benzoquinones (Kobayashi et al., 1994). Another high molecular weight ger-



66



70

Scheme 10-17.

manium containing copolymer **69** ( $M_w > 10^6$ ; GPC) was recently prepared by the combined use of a germylene **67** and thietane **68** (Shoda et al., 1996). Sundar and Keller (1996) report on linear boron-silicon-diacetylene copolymers **70**. The diacetylenic functionalities were found to crosslink

thermally to give stable networks at elevated temperatures, and the silicon and boron incorporated into the host polydiacetylenic polymers were found to enhance the oxidative stability of the material.

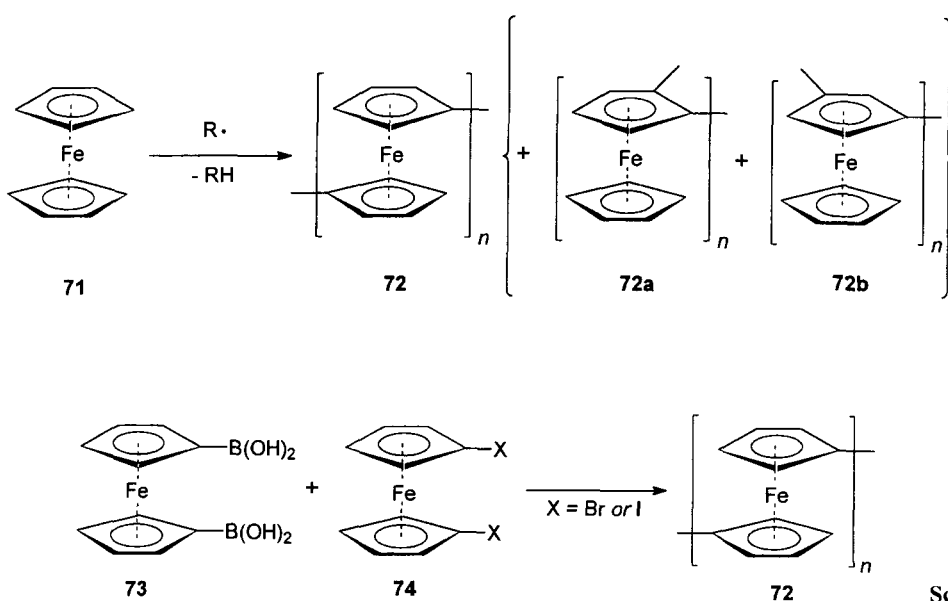
## 10.4 Polymers that have Transition Metals as Integral Parts of Their Main Chains

### 10.4.1 Poly(1,1'-metallocenylenes)

Soon after the discovery of ferrocene (Kealy and Pauson, 1951; Miller et al., 1952; Togni and Hayashi, 1994), an attempt was made to use this organometallic compound in polymer science (Neuse and Rosenberg, 1970; Neuse, 1981; Sieber, 1991; Rosenblum, 1994; Manners, 1994; Ciardelli et al., 1996). The technological interest was in particular areas such as thermal stability, radiation protection, combustion catalysis, rubber vulcanization, and redox properties. Although the preparation of polymers with metallocene-containing side groups (Pittman et al., 1970) and of polymers that contain isolated metallocenylene moieties in polyester, polyamide, or polyurethane main chains (Patterson et al., 1974; Gonsalves et al., 1984; Wright and Sigman, 1992; Wright and Toplikar, 1994)

was not difficult, it proved to be extremely hard to synthesize macromolecules in which the metallocenylene moieties are linked (*i*) directly to each other, (*ii*) via short bridges [Fe-Fe distances  $< 7 \text{ \AA}$  (0.7 nm)], or (*iii*) via  $\pi$ -conjugated comonomers. A multitude of competing side reactions which ferrocene and other metallocenes tend to undergo have hindered clean and homologous propagation steps for many years. Much effort was nevertheless invested to make such polymers available in which the ferrocenylene moieties can interact intramolecularly. They therefore, should display interesting electrical (Morrison and Hendrickson, 1975; Kramer and Hendrickson, 1980; Mueller-Westerhoff, 1986; Nalwa, 1990), magnetic (Kollmar et al., 1991; Chi et al., 1991; Hmyene et al., 1994), and optical (Wrighton, 1979; Niishikata et al., 1989; Nalwa, 1991; Wright et al., 1992, 1994) properties.

The earliest and most widely explored approach to the parent polymer poly(1,1'-ferrocenylene) **72** (Scheme 10-18) involves



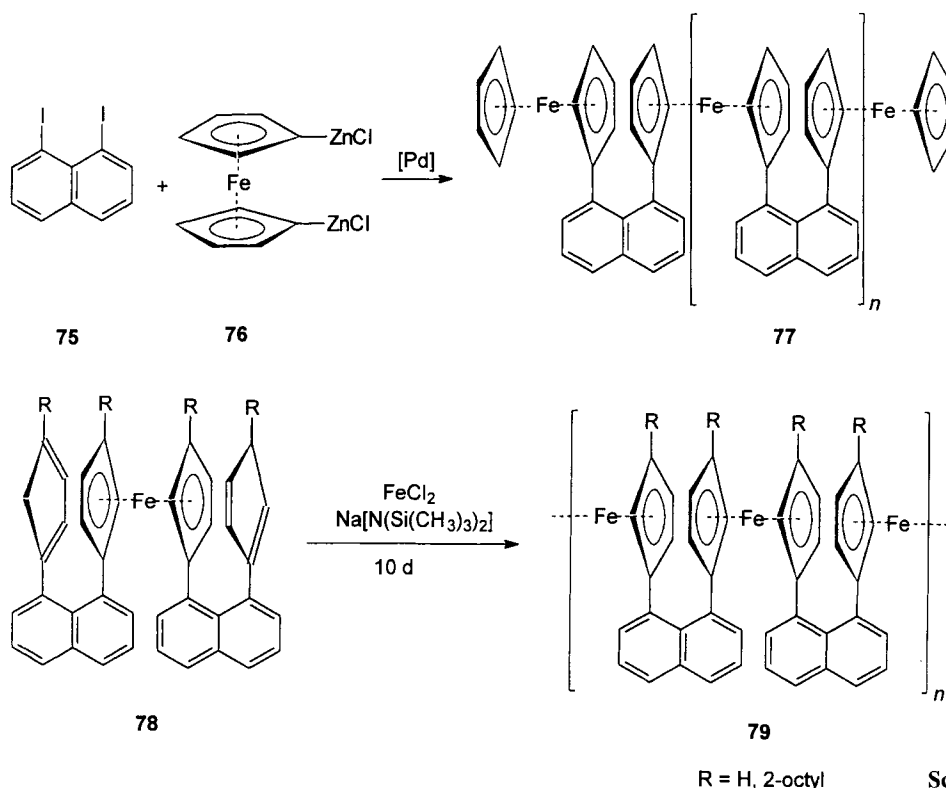
Scheme 10-18.

free radical processes (Neuse and Rosenberg, 1970; Neuse, 1981): Ferrocene radicals are generated via thermolysis of ferrocene **71** in the presence of peroxides, and polymer growth occurs via polyrecombination mechanism. However, the degrees of polymerization of **72** were typically lower than  $M_n \approx 7000$ . Moreover, all three possible constitutional isomeric constituents were present in the products as well as defects like  $\text{CH}_2$  and O groups. Finally, most products were crosslinked, clearly attesting both the lack of regioselectivity in the primary free radical attack and the potential polyfunctionality of the dicyclopentadienyl iron system. Therefore a variety of condensation reactions was tested including the Ullmann coupling of 1,1'-dihaloferrocenes (Nesmeyanov et al., 1963; Rausch et al., 1970; Rolling and Rausch, 1972), the self-condensation of chloromercuriferrocenes (Izumi and Kasahara, 1975), the oxidative coupling of dilithioferrocene (Spilners and Pellegrini, 1965; Watanabe et al., 1966; Rausch and Ciappenelli, 1967; Rausch et al., 1973; Bednarik et al., 1977), the treatment of 1,1-dilithioferrocene with 1,1'-diiodoferrocene (Neuse and Bednarik, 1979 a, b), and the conversion of 1,1'-dihaloferrocene monomers in the presence of stoichiometric quantities of magnesia (Yamamoto et al., 1983) to make constitutionally homogeneous polymers **72** with high molecular weights available. However, values of  $M_n < 5000$  were determined throughout for the soluble parts of the products, and the otherwise highly efficient palladium-catalyzed aryl-aryl coupling reaction also failed to couple ferrocene-1,1'-diboronic acid **73**, which is stable in air and water and can thus be isolated and purified, with 1,1'-dihaloferrocenes **74** ( $\text{X} = \text{Br}, \text{I}$ ) (Knapp and Rehahn, 1993 a, b; Knapp et al., 1998). Thus there has been no method so far that provides poly(1,1'-ferrocenylenes) **72** of acceptable

molecular masses and free from structural imperfections. The same applies to poly(1,1'-ruthenocenylenes), where low molecular weight materials ( $M_n < 2000$ ) are constantly obtained.

#### 10.4.2 Poly(1,1'-metalloccenylene arylenes)

Two successful strategies have been developed in the last decade for the synthesis of well-defined poly(1,1'-ferrocenylene arylenes), both taking advantage of the concept of solubilizing side chains (Ballauff, 1989). Rosenblum et al. obtained polymeric metallocenylene polydecker sandwich complexes in which the repeating metallocene units are held face-to-face by naphthalene spacers (Arnold et al., 1988; Foxman et al., 1991; Foxman and Rosenblum, 1993; Nugent et al., 1993; Rosenblum, 1994; Rosenblum and Reiff, 1995). Initially, the authors tested the palladium-catalyzed polycondensation of bis(chlorozinc)ferrocene **76** (Scheme 10-19) with 1,8-diiodonaphthalene **75** to obtain polymers **77**. However, because the formed products **77** were of rather low molecular weight ( $M_n < 4000$ ), an ameliorated coupling technique was developed where a monomeric dianion is generated in situ from compound **78**, which is subsequently reacted with  $\text{FeCl}_2$  to give the purple polymer **79** ( $M_n \approx 18000$ ) (Nugent et al., 1993; Rosenblum, 1994). When  $[\text{Ni}(\text{acac})_2]$  is used instead of  $\text{FeCl}_2$ , alternating copolymers were obtained having both iron and nickel atoms in their main chains. However, the soluble fractions of these latter polymers only have low molecular weights ( $M_n < 3000$ ) so far. Investigation of the electrical and magnetic properties of these rather unusual polymers and copolymers showed electrical conductivities of up to  $6.7 \times 10^{-3} \text{ S cm}^{-1}$  for  $\text{I}_2$ -doped materials (Rosenblum,



Scheme 10-19.

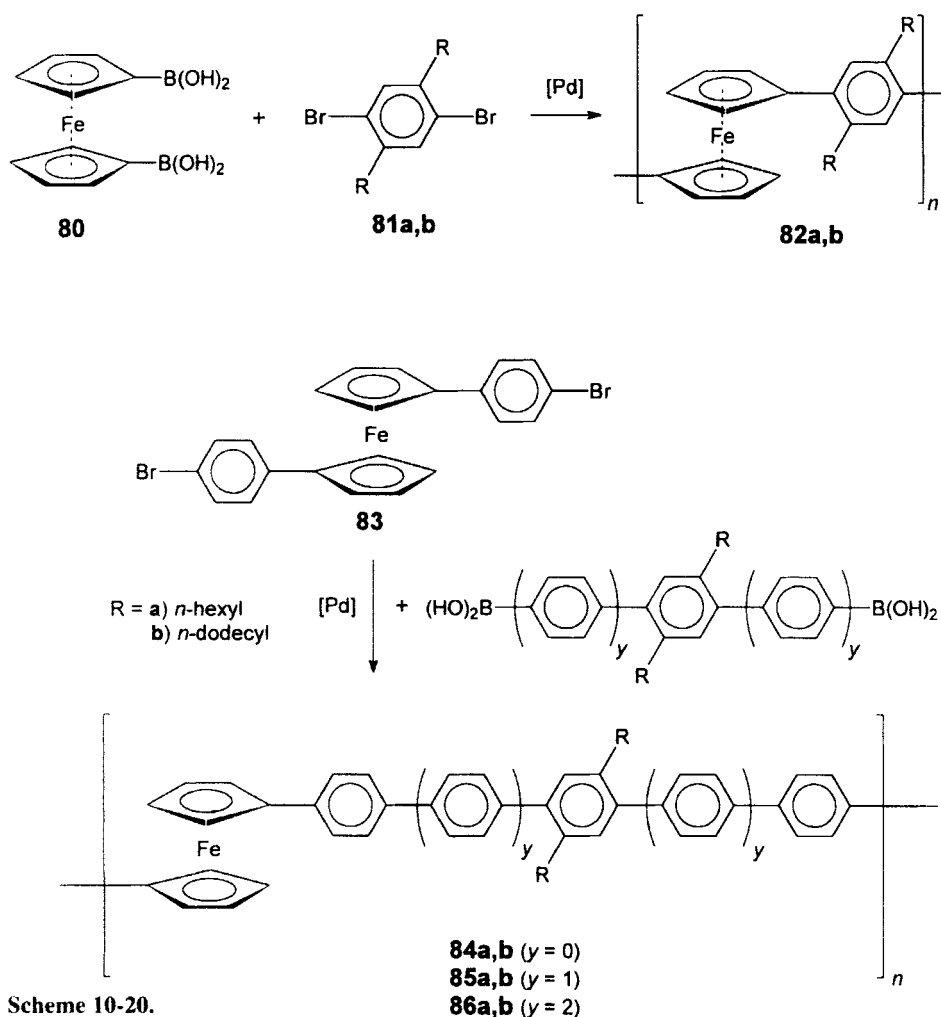
1994; Rosenblum and Reiff, 1995). From structural investigations of oligomers, it was concluded that the stacked arrays in these polymers have a helical structure (Foxman et al., 1991).

The palladium-catalyzed polycondensation reaction of haloaromatics and arylboronic acid derivatives constitutes the second successful route to well-defined poly(1,1'-ferrocenylene arylenes) (Knapp and Rehahn, 1993a, b; Knapp et al., 1998). Initially, an attempt was made to prepare poly(1,1'-ferrocenylene-1,4-phenylenes) **82** (Scheme 10-20). However, side reactions were found to prevent the formation of high molecular weight products in all polycondensations where a phenyl-ferrocenyl bond formation step was the polymer propagation

process. To circumvent this difficulty, an altered strategy was developed and indeed, high molecular weight poly(1,1'-ferrocenylene-4,4''-*p*-oligophenylenes) **84–86** were obtained when 1,1'-bis(*p*-bromophenyl)ferrocene **83** was used as the ferrocene-containing monomer. Constitutionally homogeneous polymers **84** ( $P_n \approx 55$ ), **85** ( $P_n \approx 40$ ), and **86** ( $P_n \approx 10$ ) were obtained as soluble orange solids in nearly quantitative yields.

The poly(1,1'-ferrocenylene arylenes) **84**, **85** and **86** are stable up to about 380 °C. Poly(1,1'-ferrocenylene-*p*-terphenylenes) **84** form amorphous glasses and have glass transitions at  $T_g \approx 80$  °C (**84a**) and 20 °C (**84b**), respectively. Polymers **85** and **86**, on the other hand, are semicrystalline.





Scheme 10-20.

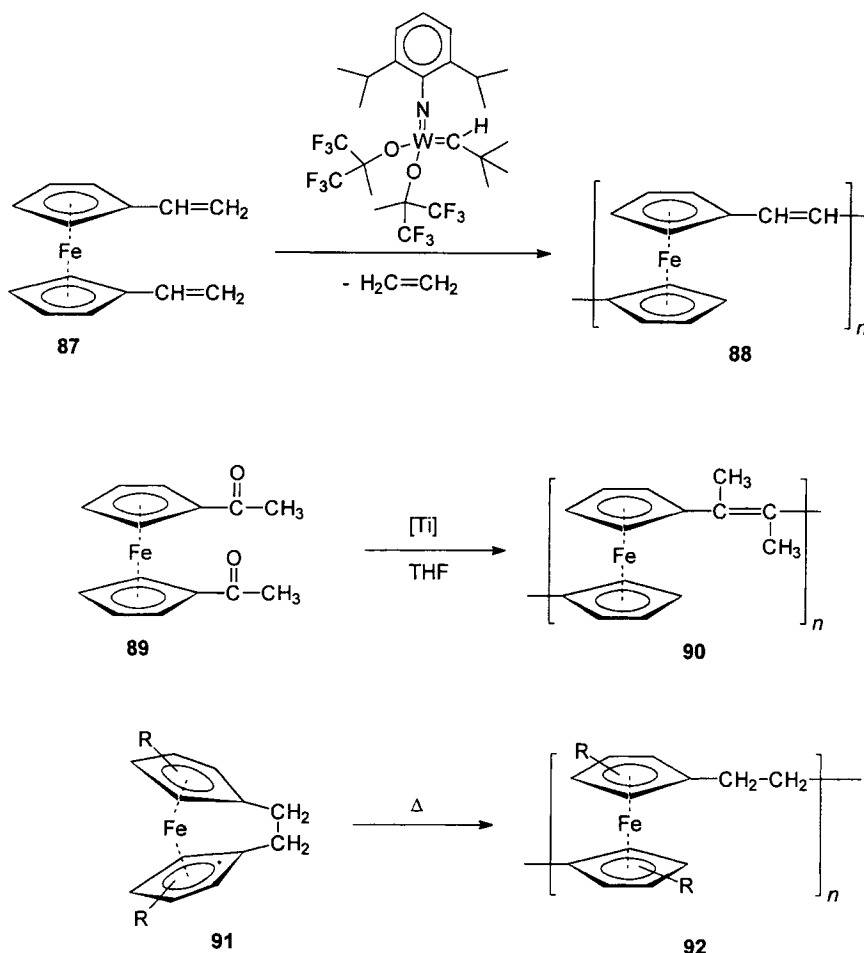
### 10.4.3 Further Poly(1,1'-metallo-cenylene) Derivatives with $\pi$ -Conjugated Bridging Units

In 1993, Gamble et al. reported the acyclic diene metathesis (ADMET) polymerization of 1,1'-divinylferrocene **87** (Scheme 10-21) to form oligomeric poly(1,1'-ferrocenylene vinylenes) **88**. Stebani et al. (1993) obtained soluble poly(ferrocenylene dimethylvinylenes) **90** via poly reductive coupling of 1,1'-diacetylferrocene **91** using low valency titanium compounds. Constitutionally homogeneous polymers **92**

having molar masses of up to  $M_w = 17\,700$  (after fractionation) were obtained.

### 10.4.4 Poly(1,1'-metallo-cenylene ethylenes)

While an efficient synthetic route for poly(1,1'-ferrocenylene methylenes) is still unavailable (Manners, 1996; Neuse and Rosenberg, 1970), the corresponding macromolecules having two carbon atoms between the ferrocenylene moieties, i.e., poly(ferrocenylene ethylenes) **92**, are avail-

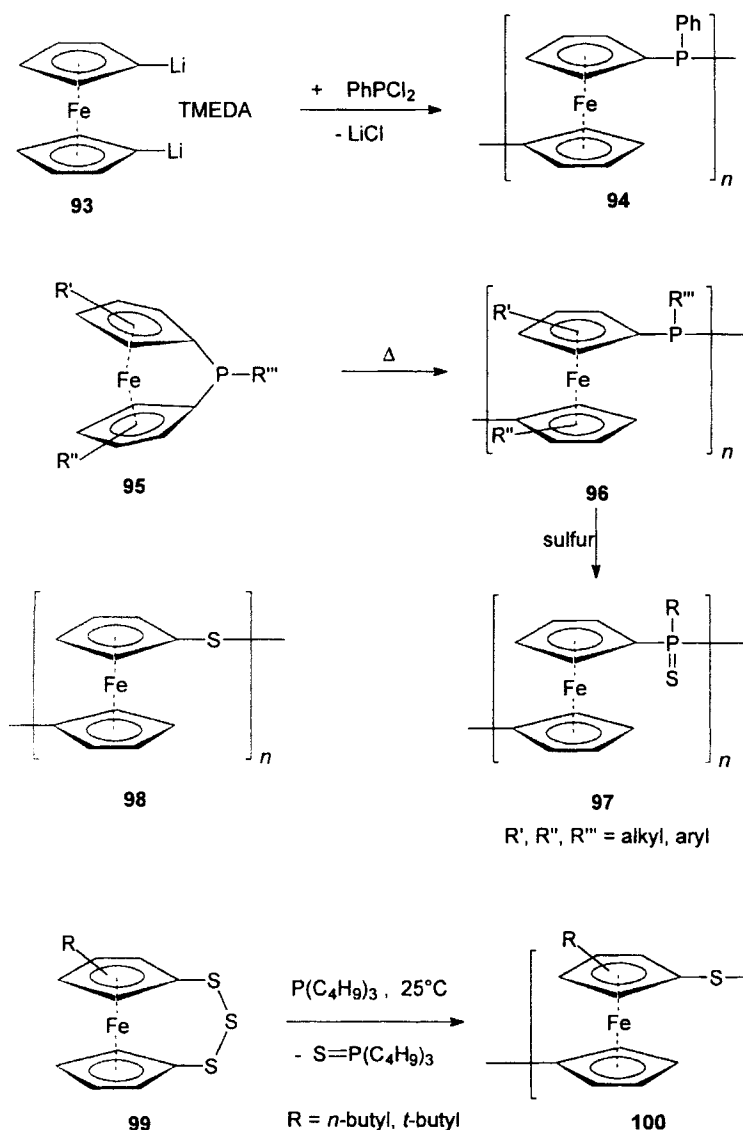


Scheme 10-21.

able in excellent yields by the recently developed thermally induced ROP synthesis of carbon-bridged [2]ferrocenophanes **91** (Nelson et al., 1993; Manners, 1994; Hmyene et al., 1994). The driving force of this polymerization is the ring strain induced by the tilt angle (approx.  $21^\circ$ ) of the two cyclopentadienyl rings of **91** (Manners, 1995). The ring strain is further increased when the larger ruthenium atom is placed into the [2]metallocenophane. Hence, hydrocarbon-bridged [2]ruthenocenophanes (tilt angle  $\approx 30^\circ$ ) can be readily polymerized as well via ROP, leading to poly(ruthenocenylene ethylenes) (Nelson et al., 1995).

#### 10.4.5 Phosphorus-, Sulfur-, and Selenium-Bridged Poly(1,1'-metallocenylene) Derivatives

Until recently, poly(1,1'-ferrocenylene phosphanes) were only available via polycondensation reactions. Among these, the most efficient route is the reaction of 1,1'-dilithioferrocene  $\times$  TMEDA **93** (Scheme 10-22) with phenyldichlorophosphine (Withers et al., 1982; Fellmann et al., 1983). Polymers **94** ( $M_w = 8900\text{--}161\,000$ ) were obtained which are thermally stable up to  $350^\circ\text{C}$ . Recently, the thermally induced ROP of phosphorus-bridged [1]ferroceno-

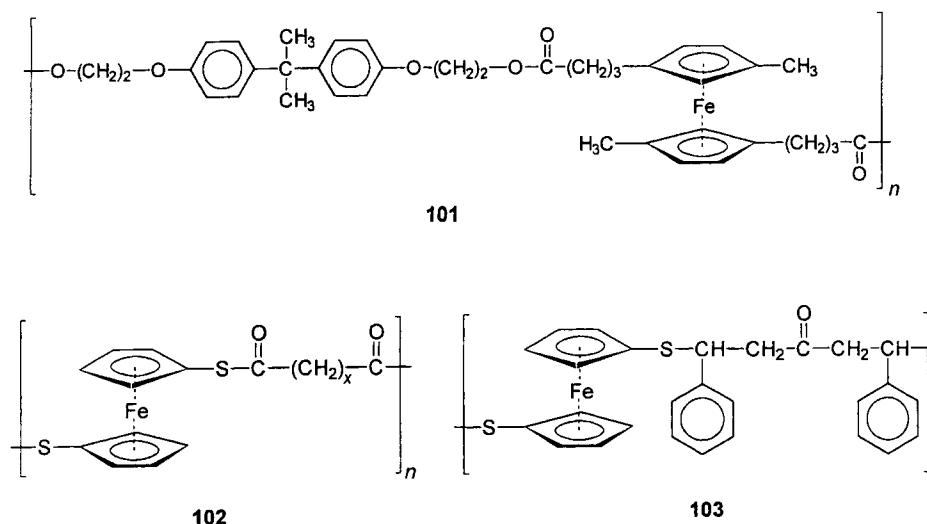


Scheme 10-22.

phanes **95** was shown to be an efficient route to poly(1,1'-ferrocenylene phosphanes) **96** and poly(1,1'-ferrocenylene phosphanesulfides) **97** (Honeyman et al., 1995). Sulfur-bridged [1]ferrocenophanes can be converted analogously to give poly(1,1'-ferrocenylene sulfides) **98** (Pudelski et al., 1995 a). More recently, Honeyman et al. (1996) also described the living anionic ROP (*n*-BuLi, THF, 25 °C) of [1]ferrocenophanes such as

**95** to yield poly(ferrocenylene phosphanes) **96** of controlled molecular mass, as well as block copolymers.

In 1992, Brandt and Rauchfuss showed that even the nearly unstrained [3]trithiaferrocenophanes **99** can be used as monomers: Poly(1,1'-ferrocenylene persulfides) **100** are formed in atom-abstraction polymerization using  $\text{PBu}_3$  as the desulfuration agent. The molecular weights of **100** depend on the



Scheme 10-23.

solvent and vary from  $M_w = 12\,000$  to  $395\,000$  (GPC). Moreover, polymers **100** are distinguished by many interesting properties (Nuyken et al., 1992; Brandt and Rauchfuss, 1992; Galloway and Rauchfuss, 1993; Compton and Rauchfuss, 1994; Compton et al., 1995). The S-S bonds, for example, can be cleaved reductively using  $Li[B(Et_3)H]$ , and reformed subsequently via oxidation with  $I_2$ . The electrochemical behavior is similar to that of poly(1,1'-ferrocenylene silanes), but the interactions between the iron centers seem to be even stronger. Finally, crosslinked polymers **100** were prepared by using [3]ferrocenophanes with two trisulfide bridges (Galloway and Rauchfuss, 1993), and linear poly(1,1'-ferrocenylene perselenides) of lower molecular weight became available upon conversion of the respective selenium-bridged monomers.

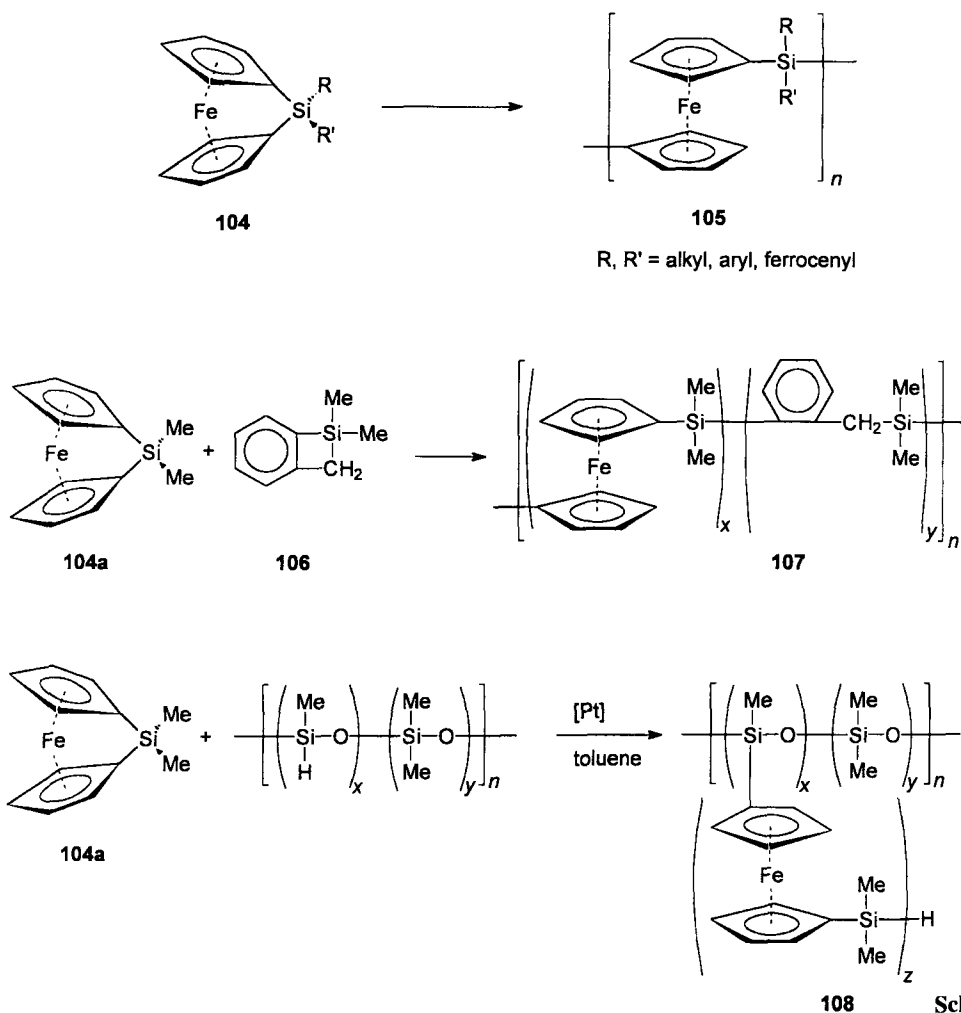
#### 10.4.6 Further Poly(1,1'-metallo-cenylene) Derivatives with Nonmetallic Bridging Units

Novel ferrocene-containing copolyesters such as **101** (Scheme 10-23) have been pub-

lished recently by Wilbert et al. (1995). In the course of these investigations it was shown that the redox potential of the ferrocenylene units increases by about 40 mV upon polyester formation. Since the ester groups are four to six  $\sigma$ -bonds away from the ferrocenylene moieties, this increase is assumed to be due to through-space charge-transfer interactions. Rheological measurements also show an unusual rubber-like behavior of the ferrocene-containing polyesters. Nuyken et al. (1996), on the other hand, prepared sulfur-containing polymers such as **102** and **103** via polyaddition of 1,1'-dimercaptoferrocene and 1,1'-bis(2-mercaptoethyl)ferrocene, respectively, to diolefinic monomers, or via polycondensation of 1,1'-dimercaptoferrocene with bifunctional acid chlorides.

#### 10.4.7 Poly(1,1'-ferrocenylene silanes) and Poly(1,1'-ferrocenylene germanes)

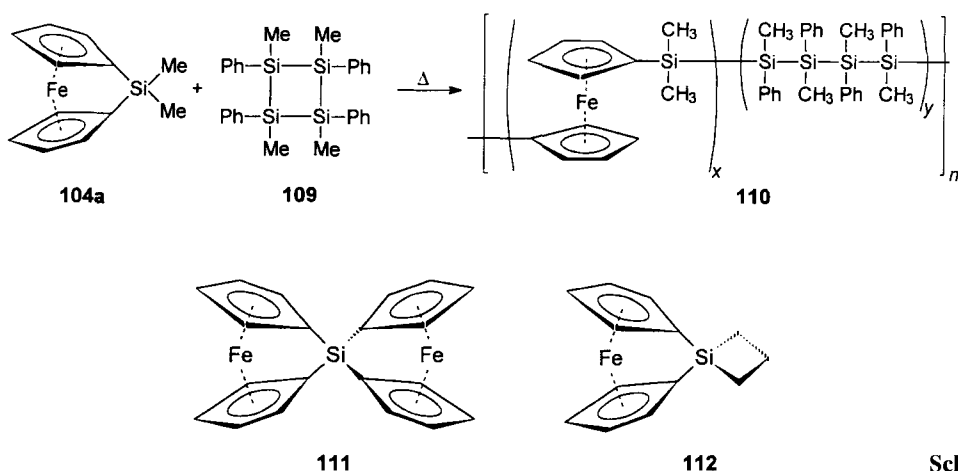
The first low molecular weight poly(1,1'-ferrocenylene silanes) **105** (Scheme 10-24) ( $M_n < 7000$ ) were prepared using polycondensation reactions (Neuse and Rosenberg, 1970; Tanaka and Hayashi, 1993; Park



Scheme 10-24.

et al., 1995). Really high molecular weight poly(1,1'-ferrocenylene silanes) ( $M_w = 10^5$  to  $10^6$ ,  $M_n > 10^5$ ), on the other hand, have been available since 1992 when Foucher et al. took advantage of thermally induced ROP for the preparation of **105** and well-defined poly(ferrocenylene germanes) (Foucher and Manners, 1993; Foucher et al., 1994 a, b). The driving force for the ROP is the ring strain in monomers like **104** ( $\approx 80 \text{ kJ mol}^{-1}$ ), whose cyclopentadienyl rings are tilted by about  $21^\circ$  towards each other.

Since then, many other silicon-bridged [1]ferrocenophanes have been prepared and polymerized analogously (Manners, 1993; Nguyen et al., 1993; Finckh et al., 1993; Foucher et al., 1993 a, b; Manners, 1994; Rulkens et al., 1994 a; Foucher et al., 1994 c; Pudelski and Manners, 1995; Pudelski et al., 1995 b; Manners, 1995; Pudelski et al., 1996; Peckham et al., 1996). Moreover, the living anionic ROP of **104** ( $n\text{-Bu-Li}$ , THF,  $25^\circ\text{C}$ ) has been found to be an efficient alternative to the thermally induced process (Rulkens et al., 1994 b; Ni et al.,



Scheme 10-25.

1996b), as the molecular weights can be predetermined, narrow molecular weight distributions can be realized, and even block copolymers are available. Another recent success is the platinum- or palladium-catalyzed ROP of [1]sila- and [1]germa-ferrocenophanes, which gives poly(1,1'-ferrocenylene silanes) **105**, poly(1,1'-ferrocenylene germanes), and copolymers thereof even at room temperature (Ni et al., 1995; Reddy et al., 1995). It also provides access to block copolymers such as **107** ( $M_n \approx 10^4$ ,  $M_w/M_n = 2.3$ ) (Sheridan et al., 1996) or graft copolymers such as **108** (Gómez-Elipé et al., 1997). Moreover, random copolymers **110** were prepared via thermal copolymerization of **104a** and **109** (Fossum et al., 1995). These polymers are expected to display interesting photophysical and charge carrier properties, and their backbone can be degraded by UV-induced cleavage of the oligosilane segments. Finally, thermotropic poly(ferrocenylene silanes) bearing 4-pentoxy-4'-hydroxyhexanoxyazo-benzene acrylate side chains have been prepared (Liu et al., 1997), spirocyclic [1]ferrocenophanes such as **111** and **112** have been found to function as crosslinking agents for poly(ferrocenylene silanes) when prepared

via the thermal ROP reaction (MacLachlan et al., 1996), and the ROP of silicon-bridged [1]ferrocenophanes with silicon-bridged bis(benzene)chromium complexes has been shown to lead to unusual dimetallic poly(1,1'-ferrocenylene silane)-poly(chrom-arylene silane) copolymers (Eschenbroich et al., 1990; Hultsch et al., 1995).

High molecular weight poly(ferrocenylene silanes) **105 a** (**a**:  $R=R'=\text{Me}$ ) display two reversible oxidations in a 1:1 ratio (Foucher et al., 1992; Rulkens et al., 1994a). This is interpreted to be the result of intramolecular electronic interactions between the metallocene centers which first cause only every second iron atom to be oxidized, and a further increase of the voltage is needed to transfer all the iron centers into  $\text{Fe}^{3+}$ . Similar behavior was also reported for other poly(1,1'-ferrocenylene silanes) (Foucher et al., 1993b; Manners, 1993; Nguyen et al., 1993; Manners, 1995). If **105 a** is doped with  $\text{I}_2$ , semiconducting materials are obtained ( $\sigma$  approx.  $10^{-7} \text{ S cm}^{-1}$ ) (Manners, 1995). The thermal behavior of polymers **105** depends on their substituents, *R*: The dimethyl derivative, for example, forms amber-colored films ( $T_m = 122^\circ\text{C}$ ,  $T_g = 33^\circ\text{C}$ ), while its di-*n*-hexyl analog is

described as rubber-like at room temperature ( $T_g = -26^\circ\text{C}$ ) (Manners, 1995; Rasburn et al., 1995). Poly(1,1'-ferrocenylene silanes) do not lose weight up to temperatures of  $400^\circ\text{C}$ , but form Fe/Si/C ceramic composites when heated up to  $500\text{--}1000^\circ\text{C}$  (Tang et al., 1993; Petersen et al., 1995; Corriu et al., 1996).

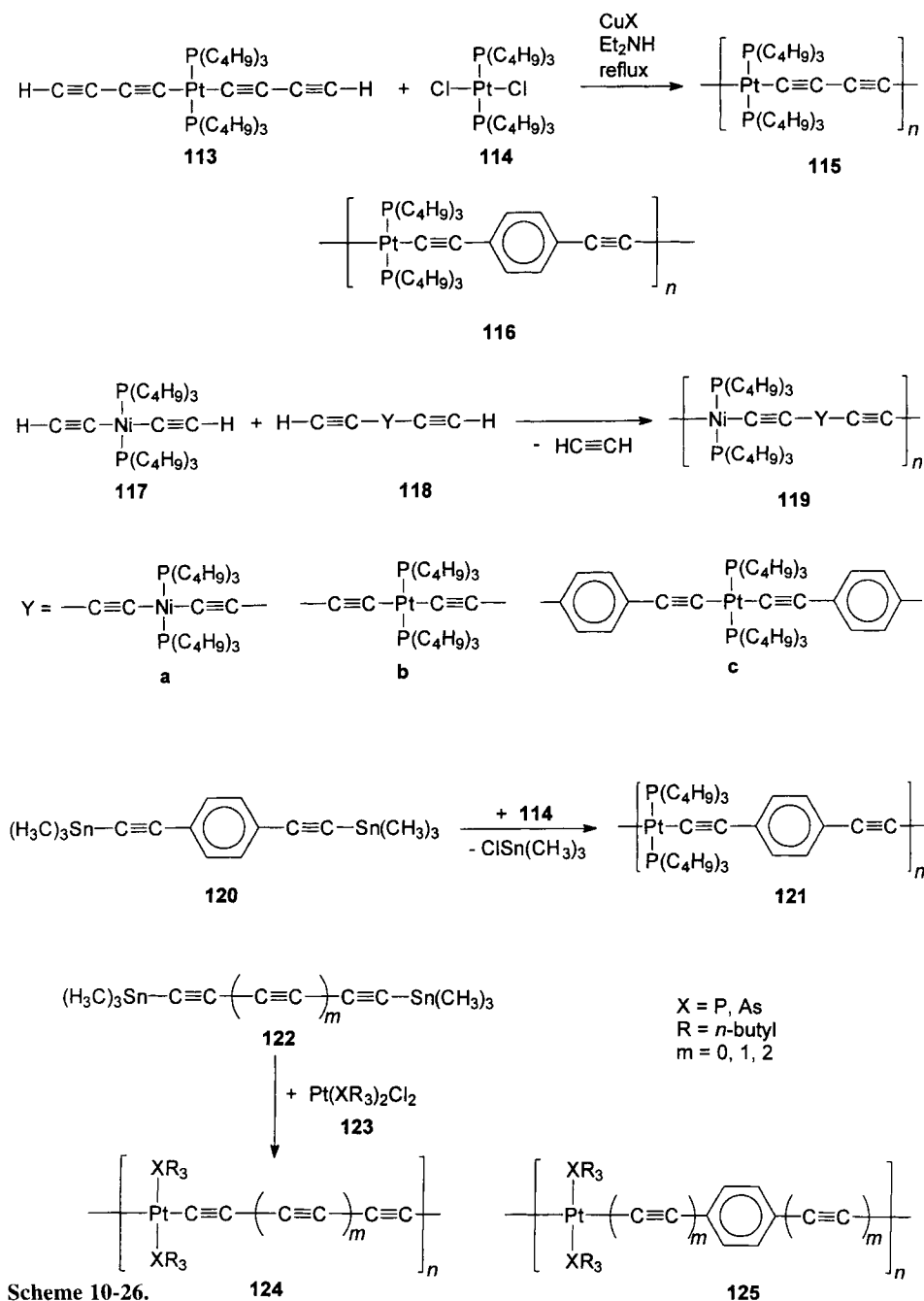
#### 10.4.8 Poly(metallaines)

In general,  $\sigma$ -bonds between a transition metal and a carbon atom are thermodynamically and kinetically unstable. Therefore it seemed unlikely for a long time that polymers held together by such bonds may be stable enough to be isolated under normal conditions. Nevertheless, some transition metal acetylide complexes were found to satisfy the prerequisites concerning the stability of the M-C  $\sigma$ -bonds (Davidson et al., 1976; Schrock et al., 1976; Hagihara et al., 1981; Ciardelli et al., 1996). Today, poly(metallaines) number among the best characterized transition metal containing polymers (Chisholm, 1991). Three copper-catalyzed methods have been developed for their preparation, i.e., dehydrohalogenation of  $\alpha,\omega$ -bisethynyl compounds (Hay, 1969; Sonogashira et al., 1977; Hagihara et al., 1981; Matsuda et al., 1984), oxidative coupling of metal-terminated oligoethynyl compounds (Takahashi, 1980), and the alkynyl-ligand exchange (Sonogashira, 1980). In 1977, Hagihara and co-workers described yellow, film-forming nickel-, palladium-, and platinum-containing polymers **115** (Scheme 10-26) of high molecular weight ( $M_w \approx 120\,000$ ,  $P_w \approx 185$ ,  $[\eta] = 2.11\text{ dL g}^{-1}$ ) (Sonogashira et al., 1977; Takahashi et al., 1978; Hagihara et al., 1981).

Soon after this success, further soluble poly(metallaines) such as **116** ( $M_w \approx 13\,000\text{--}120\,000$ ) (Takahashi et al., 1978)

were prepared analogously by the dehydrohalogenation route, i.e., via reaction of *trans*- $\text{L}_2\text{MCl}_2$  complexes ( $\text{L}$  = various phosphines,  $\text{M} = \text{Pt}, \text{Pd}$ ) with bisacetylides (Sonogashira et al. 1977, 1978; Takahashi et al., 1978, 1979; Hagihara et al., 1981; Lang, 1994). More recently (Sonogashira, 1980), high molecular weight nickel- and platinum-containing polymers **119** were obtained in good yields via the alkynyl-ligand exchange approach and thus via conversion of *trans*-bis(tri-*n*-butylphosphine)diethynylnickel **117** with  $\alpha,\omega$ -diethynyl compounds **118**. Finally, well-defined poly(platinaines) **121** ( $M_w \approx 100\,000$ , GPC) could be prepared via oxidative coupling of *trans*- $\text{PtCl}_2(\text{PR}_3)_2$  complexes like **114** with metal-terminated oligoethynyl compounds such as bis(trimethylstannyl)diins **120** (Davies et al., 1991). Analogously, high molecular weight polymers **124** ( $M_w = 96\,000\text{--}210\,000$ ) and **125** having oligoacetylenic blocks in the main chains were prepared in excellent yields as well as iron-containing polymers **128** by the application of **127** as the transition metal containing monomer (Johnson et al., 1991).

The solution properties of the above poly(metallaines) suggest that they have a rod-like structure. Mark-Houwink exponents of  $a \approx 1.7$  and independency of the intrinsic viscosity from solvent were found (Takahashi et al., 1978), and viscosity and sedimentation velocity measurements led to persistent lengths of  $l_p \approx 13 \pm 3\text{ nm}$ . Moreover, some poly(metallaines) display lyotropic nematic mesophases (Abe et al., 1991a, b), or form crystallites with a diameter of up to  $50\text{ nm}$  (Dray et al., 1992). The electronic spectra and the luminescence behavior of poly(metallaines) show the  $\pi$ -electron conjugation to be expanded over the whole polymer chain (Johnson, 1991), and the third-order nonlinear optical properties are greater than those of the corresponding

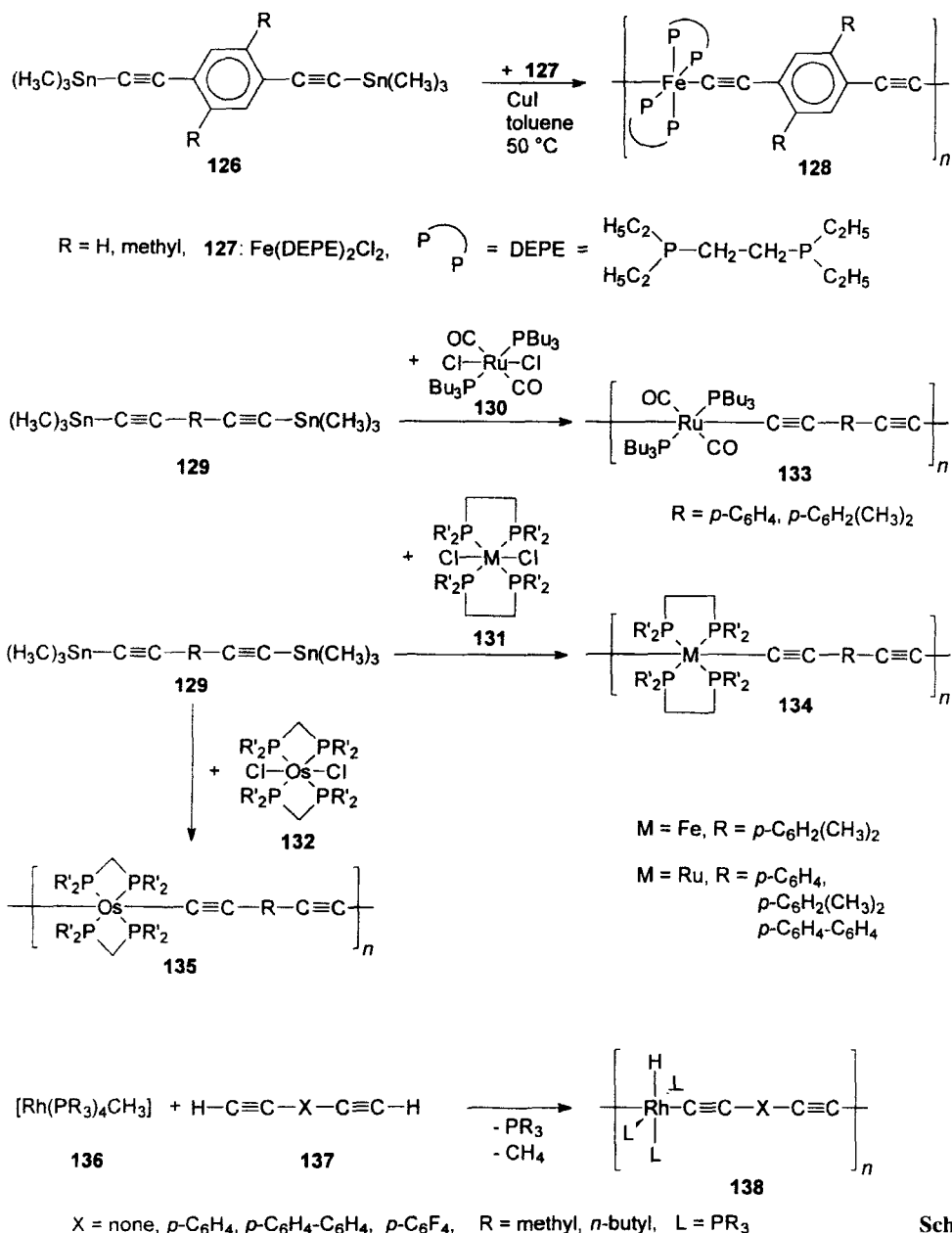


Scheme 10-26.

poly(diacetylenes) (Blau, 1991; Abe et al., 1991 b). The optical absorption and photoluminescence spectra of **124**, moreover, show a lower  $\pi$ - $\pi^*$  energy gap for triacety-

lenic than for the diacetylenic polymeric complexes. A well-resolved vibronic structure associated with the  $\text{C}\equiv\text{C}$  stretching frequency is observed for both absorption and

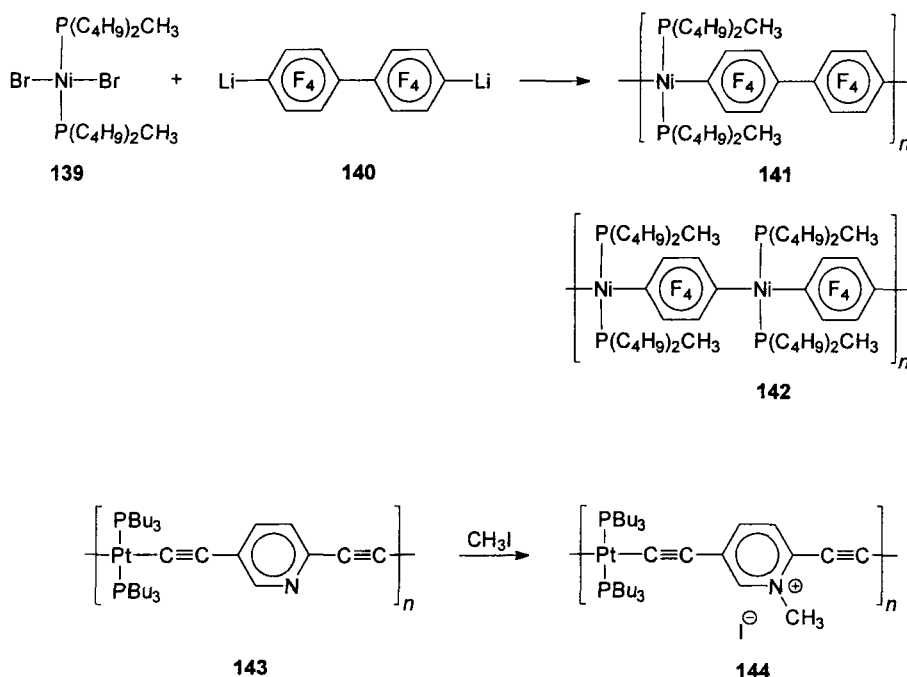




Scheme 10-27.

emission, indicating strong electron-phonon coupling for the di- and triacetylenic polymers **124** (Lewis et al., 1992; Lhost et al., 1993; Frapper and Kertesz, 1993; Khan et al., 1994a). For poly(platinaines) such as **125**, whose platinum centers are

interconnected by  $\pi$ -conjugated acetylide-arene bridges of different lengths, the band gaps for the electronic transitions in the visible range lie between 2.5 and 3.1 eV. These values are smaller than those of model complexes and are thus in full agreement with a



Scheme 10-28.

conjugation over the transition metal centers (Khan et al., 1994 a).

Recently, moreover, the synthesis and the electronic structure were described of rigid-rod octahedral iron-, ruthenium-, and osmium- $\sigma$ -acetylide complexes such as **133–135** (Scheme 10-27) (Atherton et al., 1993; Faulkner et al., 1994; Khan et al., 1994 b). In this study, the important role that the transition metal, the auxiliary ligands, and the bridging alkyne units play in determining the degree of  $\pi$ -electron delocalization in such polymers was demonstrated again. The linear arrangement of the acetylenic units around octahedral metal centers has been confirmed by single crystal X-ray structure determination performed with low molecular weight model complexes. Another interesting development is the synthesis of the rhodium-containing poly(metal-laines) **138** via the conversion of diines **137** with  $[\text{Rh}(\text{PR}_3)_4\text{CH}_3]$  **136**, which involves reductive elimination of methane and one

phosphane ligand (Fyfe et al., 1991). While the rodlike trimethylphosphane derivative is insoluble, the soluble tri(*n*-butyl)phosphane compound permitted films to be cast from THF solution. Hunter and co-workers showed that even arene-bridged organometallic polymers such as **141** and **142** (Scheme 10-28) are available via a metathesis reaction between organolithium reagents like **140** and nickel bromide complexes **139** (Sturge et al., 1992; Guo et al., 1994).

Structural elucidation was done by means of low molecular weight model complexes. The  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  NMR data suggest that, in contrast to the  $\text{C}_6\text{F}_4$ -bridged species **142**, there is no significant electronic interaction between adjacent metal centers in the  $\text{C}_6\text{F}_4$ - $\text{C}_6\text{F}_4$ -bridged complexes **141**. This suggestion is consistent with the large twist angles (ca.  $52^\circ$ ) observed between rings of the octafluorobiphenyl groups. Bunten and Kakkar (1996) describe a number of 2,5-

and 2,6-diethynylpyridine-based Pt- $\sigma$ -acetylide monomers and polymers like **143**. Quaternization of the pyridine nitrogen with methyl iodide yields stable pyridinium analogs like **144**, and is accompanied by strong red shifts in the UV-vis absorption spectra. The uncharged polymers exhibit strong fluorescence with quantum yields of 0.060–0.223. Quaternization further enhances fluorescence and quantum efficiencies. Upon doping with  $I_2$ , the polymers display semiconducting behavior.

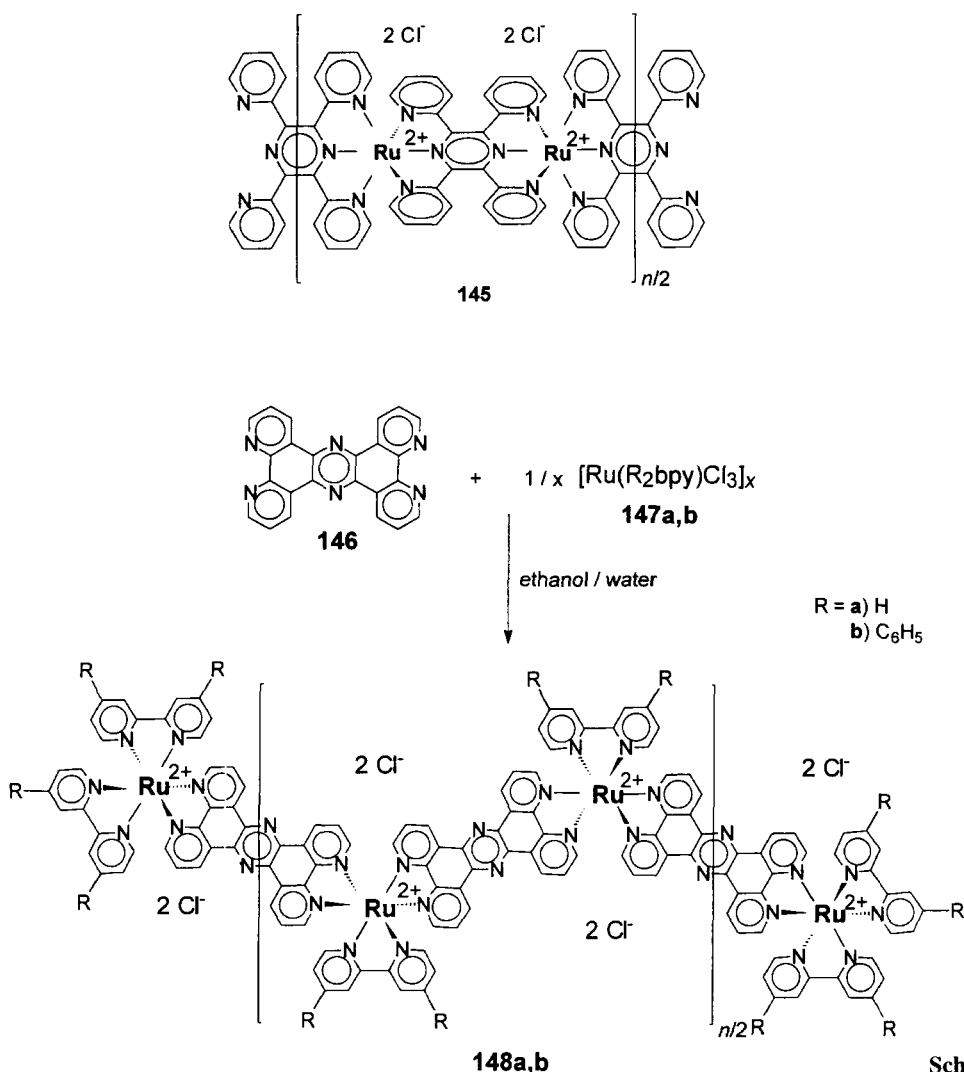
#### 10.4.9 Polymers from Octahedrally Coordinated Polyimine-Transition Metal Complexes

Multinuclear polyimine-transition metal complexes of well-defined constitution are of special interest as they may serve as model systems for the development of a profound understanding of energy- and electron-transfer processes occurring in organometallic compounds, and because of their potential technical benefit which may be based upon their unusual magnetic, electronic, and photooptical properties (Balzani et al., 1996; Harriman and Ziessel, 1996; Lehn, 1995; Ward, 1995; Sauvage et al., 1994; Denti et al., 1992 a). Ruthenium(II)- and osmium(II)-polyimine complexes may play a key role here, since they combine considerable thermal, chemical, and photochemical stability with advantageous electronic properties. Even in the early 1950s, the first macromolecular complexes like **145** (Scheme 10-29) were aimed at, but it was concluded from the rather disappointing results that such coordination polymers are hardly accessible (Goodwin and Lions, 1959). In the following decades, there was an almost complete lack of papers that deal with coordination polymers like **145**. Only in the last five years have renewed attempts

been undertaken to make such linear-chain macromolecules available. In 1996, finally, the first synthesis of readily soluble, linear ruthenium(II) coordination polymers was reported (Knapp et al., 1996; Kelch and Rehahn, 1997): Macromolecules **148** were shown to be easily available via the conversion of tetrapyridophenazine (tppz) **146** with ruthenium monomers  $[Ru(R_2bpy)Cl_3]_x$  **147** (bpy = 2,2'-bipyridine).

While the polymers **148** prepared were initially of only low molecular weight ( $P_n \approx 15$ , NMR; Knapp et al., 1996), due to a nonremovable impurity in the monomers **147**, an improved synthesis of monomers **147** finally resulted in sufficiently pure starting materials (>98%, NMR; Kelch and Rehahn, 1997) and consequently in really high molecular weight polymers **148** ( $M_w \approx 47\,000$  g mol<sup>-1</sup>,  $P_w \approx 43$ ; SAXS). Moreover, the brownish-black polymers **148** can be dissolved in a variety of solvents such as acetonitrile, ethanol, or dimethylacetamide (DMA) and, with  $Cl^-$  as the counterion, even in pure water easily and completely. In ethanol/water or DMA solution, polymers **148** display a pronounced polyelectrolyte effect when measurements are performed without a foreign salt. In the presence of a foreign salt, on the other hand, intrinsic viscosities of  $[\eta] \approx 15$  mL g<sup>-1</sup> were determined. According to the SAXS and viscosity data, polymers **148** have a rigid, randomly coiled chain conformation with densely packed chain segments. This is possible due to the random occurrence of the differently configured, chiral ruthenium(II) complexes ( $\Delta$  or  $\Lambda$  configuration) along the ribbon-like polymer backbones.

Other linear, high molecular weight coordination polymers from octahedrally coordinated polyimine-transition metal complexes have not been described so far. However, a variety of *bis*-chelating ligands exist, as well as a variety of oligomeric com-

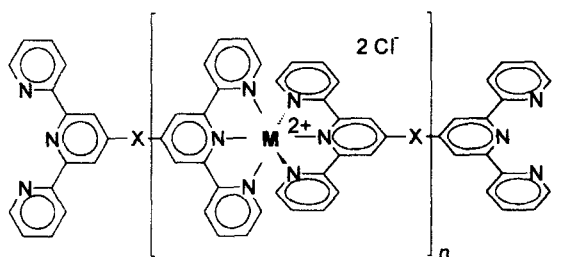


Scheme 10-29.

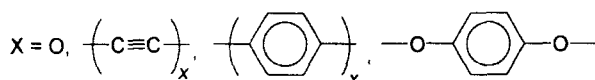
plexes. Hence it is highly probable that quite soon many further soluble, linear-chain coordination polymers will be available, such as systems like **149** (Scheme 10-30), the oligomeric species of which are currently under investigation in different research groups (see, for example, Constable et al., 1993; Barigelletti et al., 1996; Romero et al., 1996; Harriman and Ziessel, 1996; Vogler and Brewer, 1996).

On the other hand, there is a well-known, enormous variety of multinuclear complex-

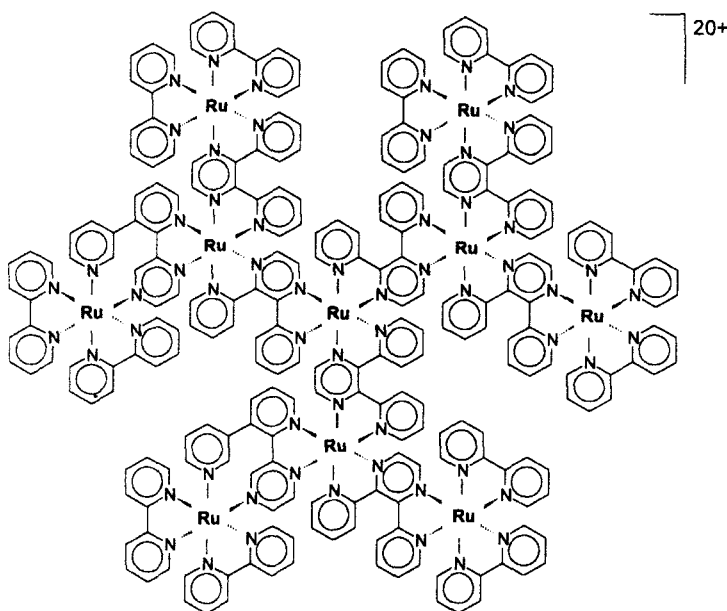
es that are branched or even dendritic, the latter being prepared both via convergent and divergent approaches (Serroni et al., 1992; Denti et al., 1992 b; Newkome et al., 1993; Achar and Puddephatt, 1994 a, b; Alonso et al., 1995; Campagna et al., 1995; Armspach et al., 1996; Constable et al., 1996 a; Constable and Harverson, 1996; Wärnmark et al., 1996; Serroni et al., 1996, 1997; Constable, 1997; Newkome and He, 1997). While in the early 1990s the largest dendrimer was the decameric complex **150**



149



M = Fe, Ru, Os, Co



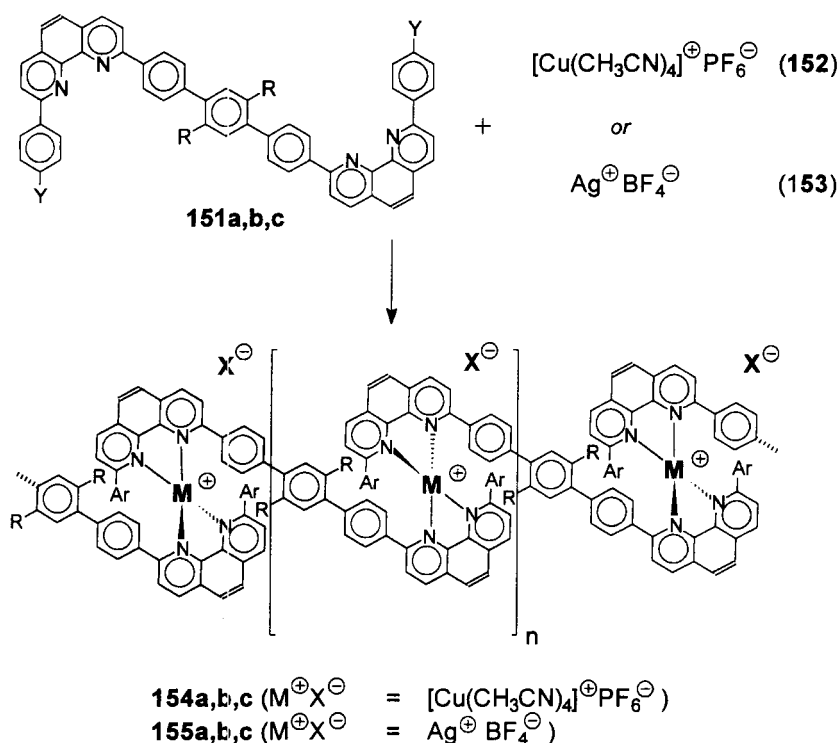
150

Scheme 10-30.

(Serroni et al., 1992), many systems are known today with approximately 20 metal centers, and the largest well-defined dendrimers have as many as 40 transition metals. Presently, the research activities are directed towards the development of even larger, well-defined coordination compounds and the profound investigation of these supramolecular species to develop reliable structure-property relationships.

#### 10.4.10 Polymers from Tetrahedrally Coordinated Polyimine-Transition Metal Complexes

As a result of the fact that tetrahedral polyimine-transition metal complexes like those of copper (I) and silver (I), widely used to build up fascinating supramolecular assemblies such as helicates, catenanes, rotaxanes, or grids [see, for example, Lehn (1990,



R = C<sub>6</sub>H<sub>13</sub>, Y = (a) H, (b) Cl, (c) OCH<sub>3</sub>, Ar = C<sub>6</sub>H<sub>4</sub>-Y

Scheme 10-31.

1995), Schneider and Dürr (1991), Amabilino and Sauvage (1996), Cárdenas et al. (1996), Constable et al. (1996b, 1997), Collin et al. (1996), Smith and Lehn (1996). Weidmann et al. (1996), Baxter et al. (1996, 1997), Meyer et al. (1997)], are kinetically unstable, they were believed until very recently to be inappropriate for the preparation of well-defined coordination polymers. In 1996, however, Velten and Rehahn developed a novel synthetic strategy that made the first soluble, constitutionally well-defined copper (I)- and silver (I)-coordination polymers available (Velten and Rehahn, 1996; Velten et al., 1997). Exclusion of even traces of (co-)solvents from the polymer solutions, which can act as competitive ligands for the metal ions, proved to be one central prerequisite for this success. To solubilize the desired polyelectrolytes in strict-

ly noncoordinating and thus rather apolar solvents, apolar *n*-alkyl side chains should also be introduced into the planned coordination polymers. Thus 4,4''-bis[(9-aryl)-2-*o*-phenanthroline]-2',5'-di-*n*-hexyl-*p*-terphenyls **151** (Scheme 10-31) were reacted with metal monomers like **152** and **153** to yield the soluble coordination polymers **154** and **155**.

After isolation from their viscous reaction mixtures as reddish-brown (**154**) or yellow (**155**) fibrous materials, the constitutionally well-defined polymers proved to be stable over months. In solution, however, "proper" coordination polymers, i.e., polymers having a constant number of repeat units per individual chain, are only guaranteed if pure halogenated hydrocarbons or acetone are used for their dissolution. Otherwise, only solution-aggregates exist, according to

NMR investigations. The precise determination of the achieved molecular weights and a profound analysis of the properties of the novel coordination polymers **154** and **155** is still outstanding.

#### 10.4.11 Schiff-Base Coordination Polymers

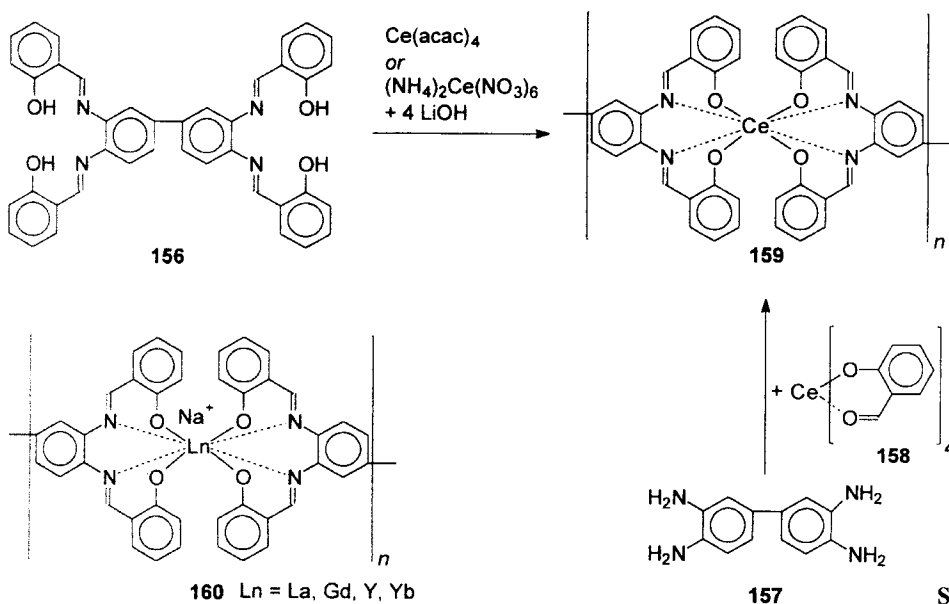
The first soluble and linear Schiff-base rare earth coordination polymers such as **159** (Scheme 10-32) ( $M_n \approx 30\,000$ ) were reported in 1994 by Chen et al. The polymers were characterized using NMR, viscosimetry, and GPC, and exhibit high thermal stability and high glass transition temperatures.

Later on, the scope of the shown strategy was broadened to other well-characterized cerium (IV) coordination polymers bearing modified ligand moieties, and lanthanoide-containing polymers such as **160**, which are polyelectrolytes (Chen and Archer, 1995, 1996; Chen et al., 1995). Some of these polymers readily dissolve in polar organic

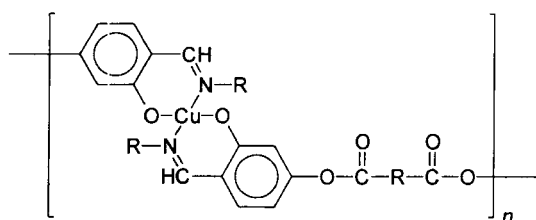
solvents such as DMSO, have molecular weights of up to  $M_n = 18\,000$ , and are expected to exhibit interesting photophysical properties.

#### 10.4.12 Further Transition Metal Coordination Polymers

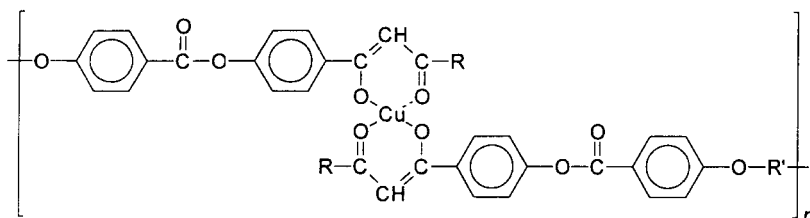
Serrano and co-workers developed liquid-crystalline polymers **161** (Scheme 10-33) which contain paramagnetic copper (II) centers within their polymer main chains (Marcos et al., 1992; Alonso et al., 1993; Oriol et al., 1994). Electron paramagnetic resonance, magnetization, and susceptibility measurements indicate that all the samples show paramagnetic behavior with a weak exchange interaction of antiferromagnetic character between the copper ions. In powdered samples, changes in magnetic properties are related to thermally induced structural modifications. Melt-drawn fibers display a large nematic order parameter. Thermotropic liquid crystalline polymers **162** linked via the bis( $\beta$ -diketonato)cop-



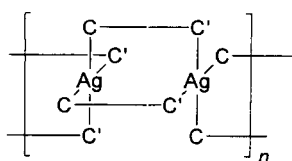
Scheme 10-32.



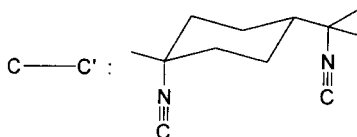
161



162



163



Scheme 10-33.

per(II) complex were furthermore reported by Hanabusa et al. (1993). Electron spin resonance (ESR) spectra of the melt-drawn fibers indicate that the plane of the square planar bis( $\beta$ -diketonato)copper(II) complex in the fiber is oriented parallel to the fiber axis. Perreault et al. (1992) reported the luminescent, silver-containing coordination polymers **163**, which are insoluble in non-polar or weakly polar solvents and water, but readily dissolve ( $60\text{--}100\text{ mg L}^{-1}$ ) in, for example, acetone, ethers, and alkyl alcohols. The Ag-Ag distance in **163** [ $\sim 5.0\text{ \AA}$  ( $0.5\text{ nm}$ )] is believed to be sufficiently large to conceive the possibility of encapsulating small monoatomic anions or cations and hence of generating chains with relatively close contacts.

Wang and Reynolds (1990) reported a new series of presumably oligomeric materials **166** and **167** (Scheme 10-34) containing nickel bis(dithiolene) linkages along their polymer main chains. A variety of flexible linkages,  $R$ , was utilized to separate the nickel complexes including O, S,  $\text{CH}_2$ ,  $(\text{CH}_2)_{10}$ ,  $(\text{CH}_2)_{22}$ , and  $(\text{OCH}_2\text{CH}_2)_3\text{O}$ . Polymers **166** with short flexible linkages are highly soluble in both aqueous and organic solvents, while the oxidized forms **167** are only slightly soluble. Increasing the length of  $R$  increases the solubility of the oxidized polymers **167**. The electrochemical and spectral properties of the polymers are consistent with a stable main chain nickel bis(dithiolene) structure where the metal complex can attain  $-2$ ,  $-1$ , and neutral oxi-

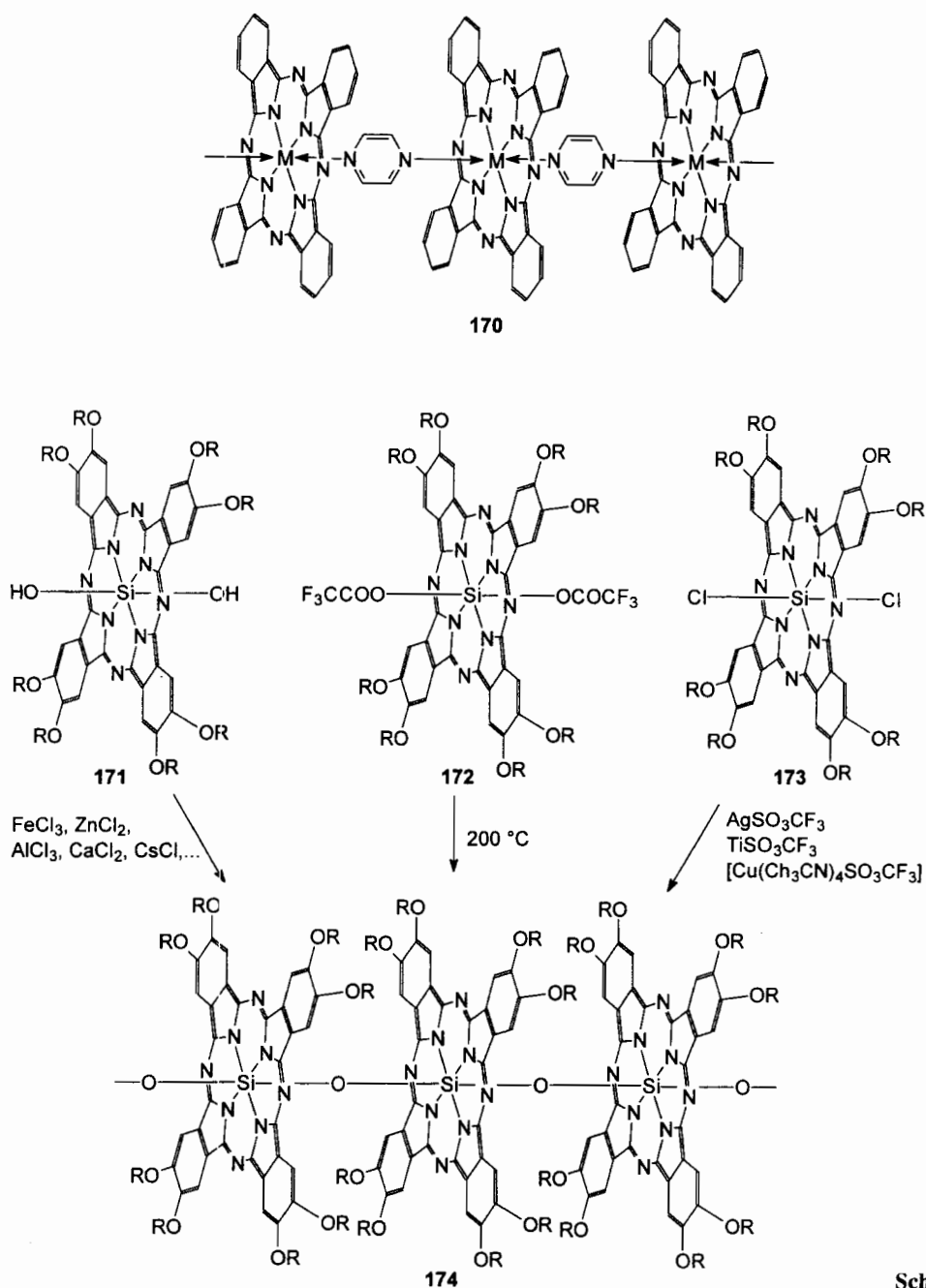




Tenhaeff and Tyler (1991, 1992) described some of the first soluble coordination polymers **168** and **169** having metal-metal bonds within their polyurethane backbones. Some of these polymers have molec-

## 10.5 Poly(phthalocyaninato)-siloxanes and Related Polymers

Bridged one-dimensional macrocyclic metal complexes containing phthalocyanine (Metz and Hanack, 1983; Schneider and Hanack, 1983; Diel et al., 1984; Hanack



Scheme 10-35.

and Münz, 1985; Kobel and Hanack, 1986), tetrabenzoporphyrine (Hanack and Hettmann-Rein, 1985), and naphthalocyanine (Deger and Hanack, 1986; Keppeler et al., 1987) as the macrocycle, a transition metal

atom, e.g. iron, ruthenium, cobalt, and rhodium, as the central metal atom, and a linear bidentate ligand such as cyanide, pyrazine, tetrazine, or 1,4-diisocyanatobenzene as the bridging ligand, are well known to ex-

hibit good semiconducting properties, even without external oxidative doping. Therefore these polymers have been widely investigated, and many excellent papers are available dealing with them (Ciardelli et al., 1996; Hedtmann-Rein et al., 1987). Moreover, transition metal containing macromolecules such as **170** (Scheme 10-35), as well as their covalently bound polysiloxane and polygermanoxane analogs, are of considerable importance as building blocks of supramolecular assemblies (Shimidzu and Iyoda, 1981; Dirk et al., 1981; Hanack and Pawlowski, 1982; Simon et al., 1984; Hanack et al. 1986; van der Pol et al., 1990; Adam et al., 1993). However, because of their rod-like main chain conformation, most of these macromolecules are insoluble and infusible materials. Therefore the concept of solubilizing side chains has been applied to these macromolecules as well, and indeed readily soluble phthalocyaninato polysiloxanes and -germanoxanes **174** having a variety of different solubilizing side groups, *R*, have been published (Metz et al., 1983; Orthmann and Wegner, 1986 a, b; Sirlin et al., 1988 a, b; Caseri et al., 1988, 1990; Sauer and Wegner, 1989, 1991; Schwiegk et al., 1991; Ferencz et al., 1993). In addition to the alkyl and alkoxy substituted derivatives, the  $\mu$ -oxo-phthalocyaninatosilicon compounds might also contain *R* groups such as methyleneoxyalkyls, crown ethers, and ester groups (Sielken et al., 1990; Kentgens et al., 1990; Crockett et al., 1990; Dulong et al., 1993 a, b).

The homogeneous molecular constitution and the rod-like shape of these "shish-kebab" polymers could be proved, and the degrees of polymerization were determined to be  $P_w = 50 - 160$  ( $M_w/M_n \approx 2$ ; SAXS) for polymers having *R* = *n*-alkyl, while for polymers bearing ester groups values of  $M_w$  as high as 360 000 ( $M_n = 140 000$ ) were reported. The rotational dynamic behavior of

polymers  $[\text{Si}(\text{O})\text{PcR}_8]_n$  was investigated in the solid state by two-dimensional NMR spectroscopy (Schwiegk et al., 1993). By this technique it was shown, for example, that the individual phthalocyanine moieties rotate round their covalent Si-O bonds rather than that the molecules as a whole rotate around their columnar axis.

Study of the phase behavior of alkoxy substituted polymers reveals the existence of three different classes of this type of polymer, depending on the side chain length (Sauer, 1993). Short side chain derivatives do not show any phase transition up to the decomposition temperature. Medium side chain derivatives show a transition to a highly viscous liquid-crystalline phase, while the long side chain derivatives have an additional fluid mesophase at higher temperatures. In all solid and liquid-crystalline phases, the rodlike molecules are packed in a two-dimensional hexagonal lattice with no discontinuous structural variations at the phase transition temperature (Sauer and Wegner, 1989; Kentgens et al., 1990; Sauer, 1993; Dulong et al., 1993 a, b). Polymers with longer side groups, *R*, were investigated with regard to their ability to form Langmuir-Blodgett (LB) films (Orthmann and Wegner, 1986 b; Crockett et al., 1990; Schwiegk et al., 1992; Ferencz et al., 1993; Dulong et al., 1993 a, b). Recently, moreover, highly ordered phthalocyaninatopolysiloxane thin films were produced on a variety of substrates using the LB thin-film deposition techniques, with coverages ranging from 1 to 100 molecular layers (Ferencz et al., 1994). These ultra-thin films show facile electron and ion transport during electrochemical and chemical oxidation, and notable stability of the phthalocyaninato cation radicals in the polymer chains in contact with both aqueous and nonaqueous media. Finally, very recently Wu et al. (1996) succeeded in directly imaging individual

shape-persistent macromolecules and their interaction by transmission electron microscopy (TEM). Cospreeding of different types of hairy rod macromolecules from a common solvent in a Langmuir trough gives two-dimensional liquid-crystalline mixtures of the constituents. Individual chains and clusters of parallel chains of the minority constituent can be clearly discerned by TEM. The micrographs thus provide hitherto unknown insights into the details of the chain-packing behavior of macromolecules close to liquid-crystal defects (disclinations).

## 10.6 Conclusions

The aim of the present chapter was to show that organic/inorganic hybrid polymers are a highly attractive, but nevertheless rather unexplored class of macromolecular materials. Since the synthesis of most of these systems is still a challenge today, only a limited number of hybrid polymers has found technical application to date, and all of them have backbones exclusively composed of main group elements. However, not only such main group systems are expected to be of special benefit for future technologies, but also those macromolecules that additionally contain transition metals: Their unusual chemical, electronic, or magnetic properties – not shown by the conventional organic macromolecules – make them potentially useful in fields like information technology, energy conversion, or catalysis. Nevertheless, for the realistic assessment of the real technological potential of this promising class of polymeric materials, reliable structure-property relationships are the basic requirement. Therefore (i) the synthetic strategies developed in recent decades must be optimized further, (ii) novel synthetic pathways have to be found,

and (iii) a profound characterization of the thus-obtained polymers is imperative. Consequently, research on soluble, constitutionally well-defined hybrid polymers is an exceptionally fruitful field of today's macromolecular research, both with regard to fundamental and materials science, and for sure the continuously increasing number of research groups working in this area will make plenty of novel and unexpected results available in the near future.

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## 10.8 References

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## 11 Chiral Polymers – The Synthesis of Optically Active Vinyl and Vinylidene Polymers with Main Chain Chirality

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## List of Symbols and Abbreviations

$m, n$	number
$M_n$	number-average molecular weight
$M_w$	weight-average molecular weight
$P_n$	number-average degree of polymerization
$r$	reactivity ratio
$[\alpha]$	specific optical rotation
$\epsilon$	extinction coefficient
$[\Theta]$	molar ellipticity
$\lambda$	wavelength
$[\Psi]$	specific ellipticity
A,B	different substituents at the main chain
AIBN	azobis(isobutyronitrile)
Ar	aryl (e.g. phenyl)
CD	circular dichroism
DDB	2,3-dimethoxy-1,4-bis(dimethylamino)butane (either (2 <i>S</i> ,3 <i>S</i> )-(+)- or (2 <i>R</i> ,3 <i>R</i> )-(–)-)
Et	ethyl
MMA	methyl methacrylate
PMMA	poly(methyl methacrylate)
PMP	( <i>S</i> )-1-(2-pyrrolidinylmethyl)pyrrolidine
TADDOL	(4 <i>R</i> ,5 <i>R</i> )-2,2-dimethyl- $\alpha,\alpha,\alpha',\alpha'$ -tetraphenyl-1,3-dioxolane-4,5-dimethanol
Trit	triphenylmethyl
UV	ultraviolet

## 11.1 Introduction

Chiral polymers comprise a very large group with different types of structure. They can be constructed of optically active building blocks forming the main chain, like their biological counterparts such as polysaccharides, polypeptides, or polynucleotides. Another possibility exists if optically active side groups are attached to an otherwise achiral polymer [for reviews on optically active polymers in general, see, Arcus (1962), Selegny (1979), Leborgne et al. (1984), Farina (1987), and Ciardelli (1987)].

Optically active polymers consisting of C–C chains with main chain chirality are more interesting from a stereochemical point of view. Their optical activity arises from the configuration of stereogenic carbon atoms in the main chain. The first examples of this type were found for 1,2-disubstituted olefins and certain substituted dienes [for reviews, see, Farina (1987), Wulff (1989)].

It was just recently that yet another type of chiral polymer was found and investigated in detail. When prochiral monomers such as vinyl or vinylidene monomers are polymerized with asymmetric induction, optically active polymers with main chain chirality are obtained [see, Wulff et al. (1978, 1987), Okamoto et al. (1979), Wulff and Hohn (1982), and reviews, Wulff (1989, 1991 a, b), Okamoto and Nakano (1994)]. This optical activity can only be produced under very special structural requirements. Though formally asymmetric carbon atoms are generated during chain growth polymerization, this does not usually result in optical activity, even if only one optical antipode is obtained. Therefore, for a long time, it was principally thought to be impossible to generate optical activity in these polymers due to the chiral configuration or conformation of the main chain (main chain

chirality) (Arcus, 1962; Pino, 1965; Goodman et al., 1967).

Incidentally, vinyl or vinylidene polymers are economically the most important and constitute a large segment of industrial applications. It is of great scientific and practical interest to incorporate chirality and optical activity into polymers of this type, since it might add specific unprecedented properties to these materials.

In this chapter, the discussion of chiral polymers will concentrate on vinyl and vinylidene polymers because these are used most frequently. Furthermore, only polymers with main chain chirality will be discussed, since the most remarkable progress during recent years was found for this group. The stereochemical background of their syntheses is somewhat complicated and not found in the usual textbooks, so this chapter begins with a short overview of the symmetry properties of polymer chains. This is followed by the description of syntheses of optically active polymers which owe their chirality to the configuration in the main chain. Another group of polymers discussed are those with optical activity caused by the chirality of a rigid conformation of the main chain, such as single-handed, helical poly(trityl methacrylate). Chiral crosslinked polymers (due to asymmetric crosslinking) will not be discussed in this chapter. They can be prepared by an imprinting procedure using chiral template molecules during the crosslinking step, followed by removal of the template afterwards (Wulff et al., 1973). This procedure leads to chiral microcavities of a specific shape and with an arrangement of functional groups complementary to the template. This research area has been reviewed recently by different groups (Wulff, 1995; Mosbach, 1994; Shea, 1994).



## 11.2 Stereochemical Considerations for the Synthesis of Chiral Polymers

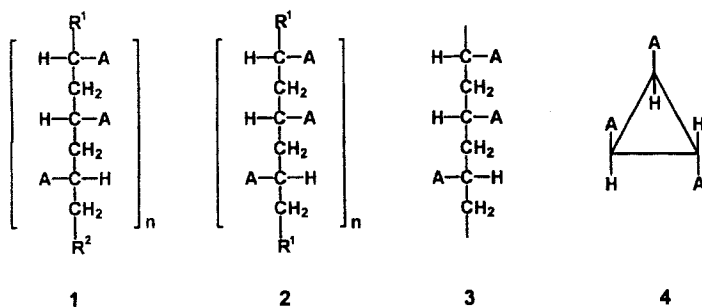
Chirality and optical activity are well-documented properties of low molecular weight compounds, especially natural products. A molecule is said to be chiral if its image and mirror-image are not superimposable. In most synthetic methods, both antipodes (enantiomers) are obtained in equal proportion (racemic mixture). In the majority of cases (but not necessarily), a pure antipode (enantiomer) exhibits optical activity, i.e., the plane of linearly polarized light is rotated during its passage through a solution of this compound. Compounds containing asymmetric carbon atoms are classical examples of chiral substances.

We will now discuss which polymers can be expected to be optically active due to main chain chirality (Wulff, 1989). Since chirality is a necessary but not a sufficient condition for optical activity, polymeric structures are first theoretically inspected for their chirality, i.e., their symmetry properties will be examined. Here, the symmetry properties of polymers of 1-substituted olefins ( $\text{CH}_2=\text{CHA}$ ) and of nonsymmetric 1,1-disubstituted olefins ( $\text{CH}_2=\text{CAB}$ ), which have the same symmetry properties, are discussed together. The symmetry consideration of these polymers is not as straightforward as with low molecular weight compounds. Even the so-called ster-

eregular polymers are never completely regular in reality, and thus it is necessary to use a model of the polymer chains, assuming that they possess an ideal stereoregular structure, i.e., that they are made up of repeating units with identical constitution and configuration. They can be best described by specifying the smallest regularly repeating configurational unit (called dyad, triad, etc.).

The second problem is concerned with the end groups. A chain composed of triads like **1**, with nonidentical chain ends, is in principle chiral. In practice, it is to be expected that with very long chains the difference between the end groups becomes negligible and hence the compound behaves like an achiral compound **2**. The compound **1** can then be called *cryptochiral* since no chiroptical properties can be measured (Mislow and Bickart, 1977; Green and Garetz, 1984). It is an interesting question, whether or not such compounds can be synthesized, and at what chain length chirality turns into cryptochirality. This will be discussed for isotactic chains in a later section (Sec. 11-4).

For very high molecular weight polymers, the end groups can be totally neglected, since they do not affect the properties of the polymer to a measurable extent. The model of the infinite chain (endless chain) **3** is then applicable. This has been demonstrated to be particularly valuable for stereochemical considerations of macromolecules. All the units of a stereoregular poly-



mer of **3** are exactly identical and there are no longer any end groups. For symmetry considerations, an infinite chain can be replaced by a ring containing the stereogenic centers of the smallest repeating unit. This ring may be regarded as an endless chain with a finite number of units (see **4** as a model of **3**) (Farina et al., 1965; Wulff, 1989).

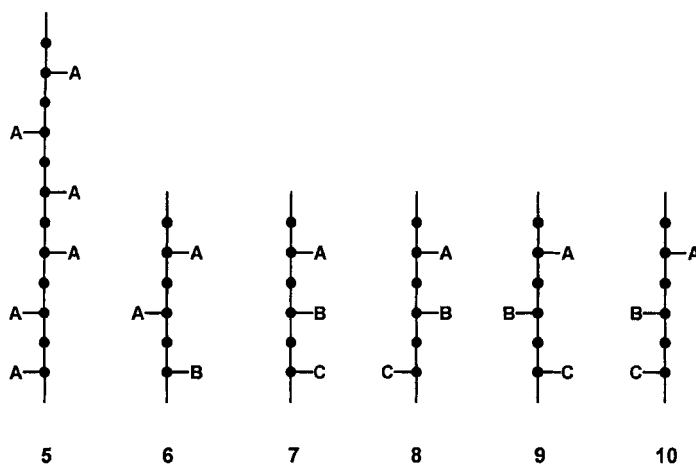
It has long been known that the three kinds of typical polymer chain arrangements, i.e., atactic, isotactic, and syndiotactic depending on the model used, are cryptochiral or achiral and are not able to show optical activity. The same also holds good for stereoregular, alternating copolymers so long as only dyads and tetrads are taken into account. On the basis of these observations, it was subsequently concluded that generally all the polymers obtained from 1-substituted or unsymmetrical 1,1-disubstituted olefins cannot be optically active.

Several years ago, we initiated a systematic analysis of the symmetry properties of different structural types present in vinyl homo- and copolymers [Wulff et al. (1978, 1987), Wulff and Hohn (1982), and reviews, Wulff (1989, 1991 a, b)]. The surprising result was that there are indeed many structures possible for stereoregular polymers which exhibit chirality due to the configu-

rational arrangements in the main chain. If these structures can be obtained as individual optical antipodes, they should be optically active. Hence the prevailing belief regarding the impossibility of obtaining optically active vinyl polymers due to main chain chirality needed to be changed.

The inspection of all possible stereoregular structures for homopolymers represented by dyads to pentads showed them to be achiral according to model **3**. On the other hand, one repeating unit of six monomers out of eight possible hexads is chiral. Polymer **5**, which is built up of such hexads, should thus be able to show optical activity.

In contrast, many more of the stereoregular arrangements are chiral in copolymers. While in alternating copolymers both possible stereo-arrangements for dyads are achiral, in stereoregular copolymers, which are built up of triads, one out of three possible arrangements is chiral (**6**). All four possible triads **7–10** in a stereoregular terpolymer are chiral. With more complex arrangements, the number of chiral configurations increases steadily. In longer repeating units of stereoregular copolymers, the vast majority of structures is chiral and should be obtainable in optically active form.

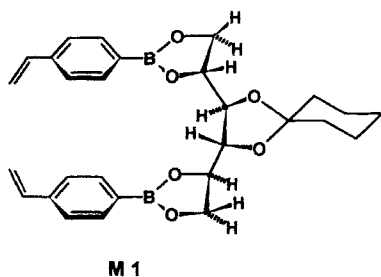


In order to prepare these tailor-made structures as pure or enriched optical antipodes showing optical activity, strategically designed efficient synthetic schemes needed to be developed. The following paragraphs describe some of the examples of this venture.

### 11.3 Syntheses of Copolymers with Chirality of the Main Chain

#### 11.3.1 Copolymers Prepared with Template Monomer **M1**

The first attempt to prepare optically active polymers with main chain chirality was aimed at regular copolymers consisting of type **6** triads (Wulff et al., 1978, 1987; Wulff and Hohn, 1982). To achieve such triads, we fixed two monomeric units in a definite geometry on a chiral template molecule and tried to copolymerize the resulting template monomer with various other vinyl monomers. After polymerization, the template molecule was intended to be removed quantitatively from the polymer to yield the desired chiral polymers.



Towards, this end, 3,4-*O*-cyclohexylidene-*D*-mannitol-1,2,5,6-bis(4-vinylphenyl boronate) **M1** was copolymerized by free radical initiation, e.g., with methyl methacrylate as a typical comonomer (see Scheme 11-1). After a conversion of

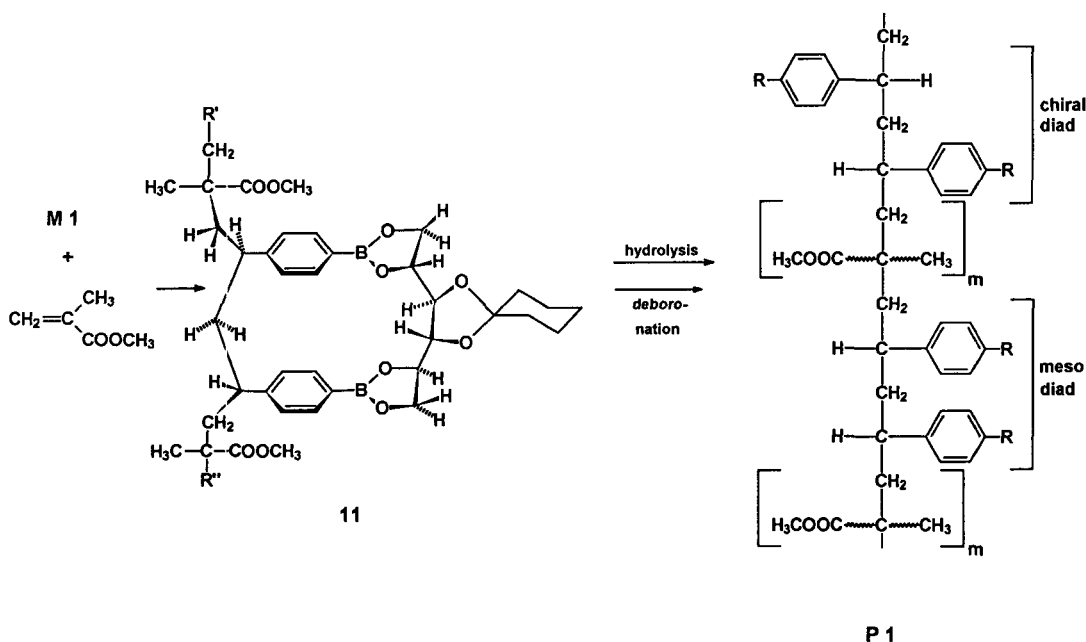
**Table 11-1.** Optical rotation of copolymers of **M1** with different comonomers after removing the template.

No	Comonomer	Mol fraction of <b>M1</b> in copolymer	$[\alpha]_{365}^{20}$ (degrees)
1	methyl methacrylate	0.27	–85
2	methacrylonitrile	0.28	–85
3	styrene	0.40	–40
4	4-aminostyrene	0.49	–9
5	4-chlorostyrene	0.58	+1.5
6	4-cyanostyrene	0.52	+27
7	4-vinylbiphenyl	0.65	+90
8	4-vinylstilbene	0.65	+145

10–20%, soluble linear polymers were obtained, indicating that some sort of cyclopolymerization must have taken place. After complete removal of the chiral template (3,4-*O*-cyclohexylidene-*D*-mannitol) from the polymer (by repeated reprecipitation from acetone/water 9 : 1 in slightly acidified water), a copolymer of 4-vinylphenyl boronic acid with methyl methacrylate (**P1b**) was obtained with a molecular weight of 80 000–100 000 g/mol showing appreciable optical activity (see Table 11-1).

Polymerization was usually stopped at 10–20% conversion to ensure uniform copolymers. It can also be polymerized to 100% conversion, which results in polymers of similar optical rotation (Wulff and Hohn, 1982).

Detailed studies on the mechanism of this asymmetric copolymerization have shown (Wulff et al., 1987) that **M1** undergoes a cyclopolymerization involving a nineteen-membered ring **11** (see Scheme 11-1). The 4-vinylphenyl boronic acid dyads thus obtained are mainly in (*S,S*)- and (*R,S*)-configuration. These configurational assignments are based on conformational analysis of the transition state of the polymerization reaction and have also been unambiguously as-



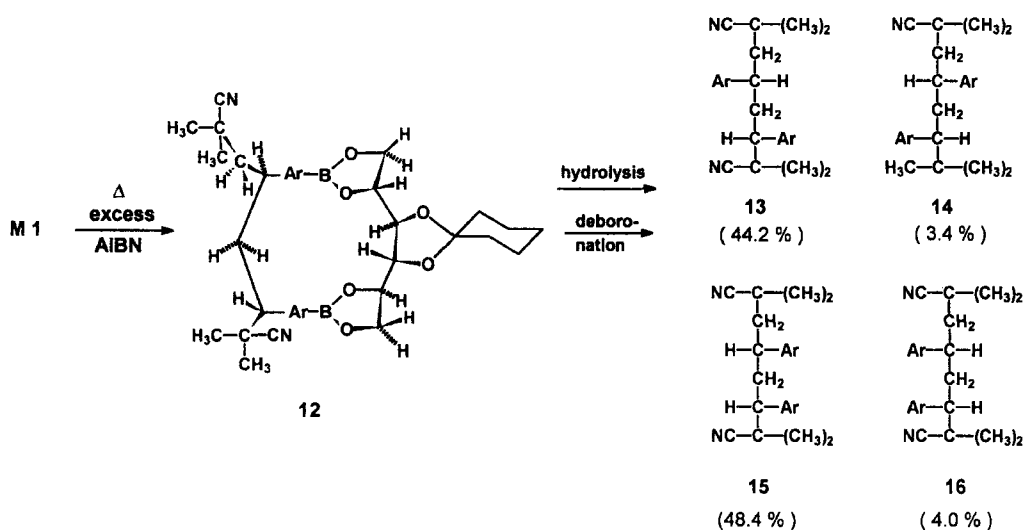
**Scheme 11-1.** Schematic representation of the asymmetric cyclocopolymerization of **M1** with methyl methacrylate. In the formula of the initial cyclization product **11**, only one stereoisomer is presented. In the formula of the open chain polymer **P1**, the two main dyads [meso dyad and (*S,S*)-dyad] in the chain are shown. [**P1a** R = H, **P1b** R = B(OH)<sub>2</sub>.]

certained by the synthesis of suitable model compounds.

A more detailed picture of the stereochemical course of the reaction was only recently obtained (Wulff et al., 1994c; Wulff and Kühnweg, 1996). Radically initiated cyclization of **M1** with an excess of azobis(isobutyronitrile) furnishes the monomeric cyclization product **12** in good yields. This reaction is a good model for the stereochemical course of the asymmetric cyclocopolymerization involving **11** with, e.g., methyl methacrylate. Unlike in a polymer **11** or **P1**, the stereoisomers in **12** can easily be determined. The template molecule as well as the boron could easily be removed from cyclization product **12**, resulting in the stereoisomers **13**, **14**, **15**, and **16** (see Scheme 11-2). Their ratio was determined quantitatively to be **13** 44.2%, **14** 3.4%, **15** 48.4%, **16** 4.0%. This means that two dia-

stereomers are formed in nearly equal amounts. Dimers **15** and **16** represent a meso dyad in a polymer and will not contribute to the optical activity. Isomers **13** and **14** represent the chiral dyad with an enantiomeric excess of 85.7%. The same distribution of dyads is expected in the polymer. Now for the first time, the ratio of the different dyads in the polymers can be deduced from these experiments.

A large variety of different comonomers can be used for the asymmetric cyclocopolymerization with **M1**. After splitting off the template, copolymers with appreciable optical activity are obtained (for some examples, see Table 11-1). The rotations have strong negative to strong positive values depending on the nature of the comonomers. Interestingly, it could be shown that all copolymers, regardless of their sign of rotation, possess the same absolute configura-



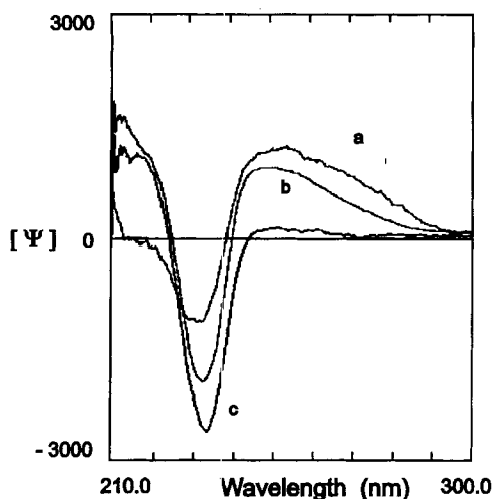
**Scheme 11-2.** Schematic representation of the radical cyclization of **M1** with azobis(isobutyronitrile) (AIBN) and the preparation of dimers **13–16**. For the cyclization only one stereoisomer is represented, whereas all four possible stereoisomers of the dimers are shown (Ar=phenyl) (Wulff and Kühneweg, 1996).

tion (*S,S*) for the (4-vinylphenyl) boronic acid dyads (Wulff and Dhal, 1988). This was shown by a chemical transformation of the copolymer of 4-cyanostyrene into a copolymer of 4-aminomethylstyrene, which turns the positive optical rotation of  $+27^\circ$  into a negative one of  $-9^\circ$ . A similar rotation was also obtained by direct copolymerization of a derivative of 4-aminomethylstyrene (see Table 11-1). Therefore (*S,S*)-distyryl dyads are present in both cases.

It appears that the optical rotation as well as the circular dichroism (CD) of copolymers composed of (*S,S*)-[(4-vinylphenyl)boronic acid] dyads and comonomers of different types can be influenced by both comonomeric partners (Wulff and Dhal, 1990). If the comonomer does not possess a UV absorption band above 210 nm (as with methyl methacrylate or methacrylonitrile), optical rotation and CD are determined by the (*S,S*) dyads. These copolymers are strongly negatively rotating and show a strong negative Cotton effect at 233 nm. The rotational power per unit is the highest

if the (*S,S*)-dyads are isolated in the chain. Therefore the maximum optical rotation is at a mole fraction of 0.25–0.30 for the chiral dyads. Comonomers that have strong UV absorption above 250 nm (e.g., 4-vinylbiphenyl) often cause an additional positive Cotton effect (see Fig. 11-1) and give rise to positively rotating polymers (see Table 11-1, entries 7 and 8). The comonomeric units show the strongest influence on the chiroptical properties if they are present as isolated units along the main chain. The highest optical (positive) rotations of the copolymers are obtained when the mole fraction of the chiral dyads is 0.65.

Figure 11-1 shows the CD of the copolymer of 4-vinylbiphenyl with 4-vinylphenyl boronic acid dyads. The strong positive Cotton effect at 255 nm is due to the aromatic chromophore; the negative one is due to the (*S,S*)-distyryl dyads. If the aromatic chromophore is more remote from the chiral backbone, its influence on the chiroptical properties becomes less effective. Copolymers of 4-biphenyl methacrylate still show



**Figure 11-1.** Circular dichroism of copolymers of **M1** with (a) 4-vinylbiphenyl, (b) 4-biphenyl methacrylate, and (c) 4-biphenylmethyl methacrylate (Wulff and Dhal, 1990).

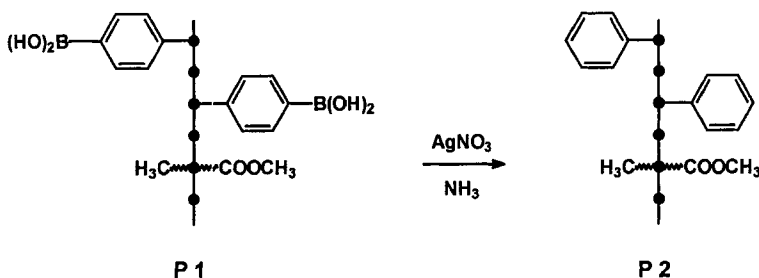
a positive Cotton effect, whereas those of 4-biphenyl-methyl methacrylate do not.

As a result of borderline cases, as in copolymers having comonomers with UV absorption between 210 and 250 nm, all optical rotations between strongly negative and strongly positive can be obtained depending on the chemical structure of the comonomers (see Table 11-1). The asymmetry of the comonomer chromophore clearly does not arise from the configurational arrangement of these units in the main chain, but by a conformational perturbation through the neighboring (*S,S*) dyads (Wulff and Dhal, 1990).

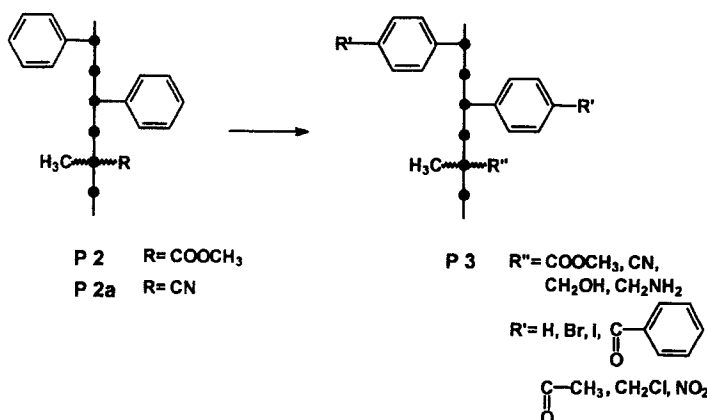
The boronic acid can be removed easily and quantitatively from all optically active copolymers. Treatment with  $\text{AgNO}_3/\text{NH}_3$  transforms the copolymer of 4-(vinylphenyl) boronic acid and methyl methacrylate into poly(styrene-*co*-methyl methacrylate) (**P2**, see Scheme 11-3), a very common and structurally simple copolymer. In this way, styrene copolymers can be derived from all our copolymers.

Polymer-analogous reactions allow us to further modify these optically active copolymers. Different reaction pathways made it possible to introduce 4-bromo, 4-iodo, 4-benzoyl, 4-acetyl, 4-chloromethyl, and 4-nitro substituents in good yields on the phenyl ring of the styrene dyad. The comonomeric part (e.g., from acrylonitrile or methyl methacrylate) can also be modified. Some examples of modifications are shown in Scheme 11-4 (Wulff and Dhal, 1987; Dhal, 1992).

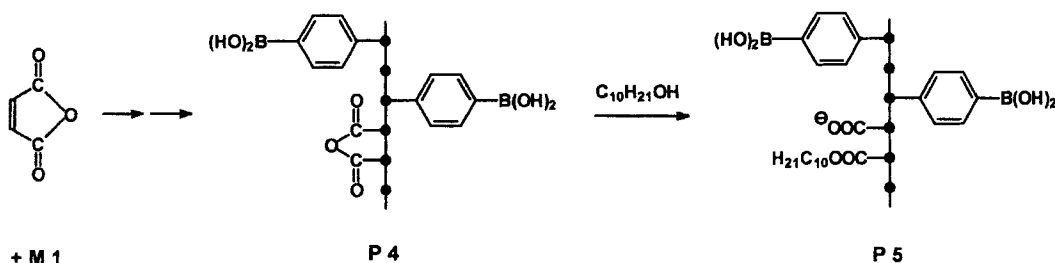
To obtain a copolymer of defined composition, the polymerization has to be stopped after 10–20% conversion since, due to the higher reactivity of **M1**, it prefers to be incorporated in the polymer [for example, copolymerization reactivity ratios for **M1** (1) and methyl methacrylate (2) are  $r_1=1.33$ ,  $r_2=0.22$ ]. In contrast, almost complete alternating copolymerization was observed when **M1** was copolymerized with maleic anhydride or *N*-substituted maleimides, which gave strictly alternating copolymers of type **P4** (Scheme 11-5) (Wulff and Krieger, 1994 a).



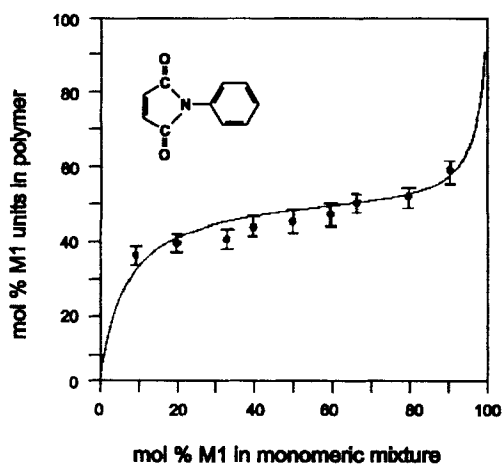
**Scheme 11-3.** Deboronation of polymers of type **P1** with  $\text{AgNO}_3/\text{NH}_3$  (Wulff et al., 1987).



**Scheme 11-4.** Polymer-analogous modifications of deboronated copolymers of **M1** and methyl methacrylate and **M1** and methacrylonitrile (Wulff and Dhal, 1987).



**Scheme 11-5.** Copolymer **M1** and maleic anhydride (**P4**) reaction with decanol and removal of the template (**P5**) (Wulff and Krieger, 1994 a).



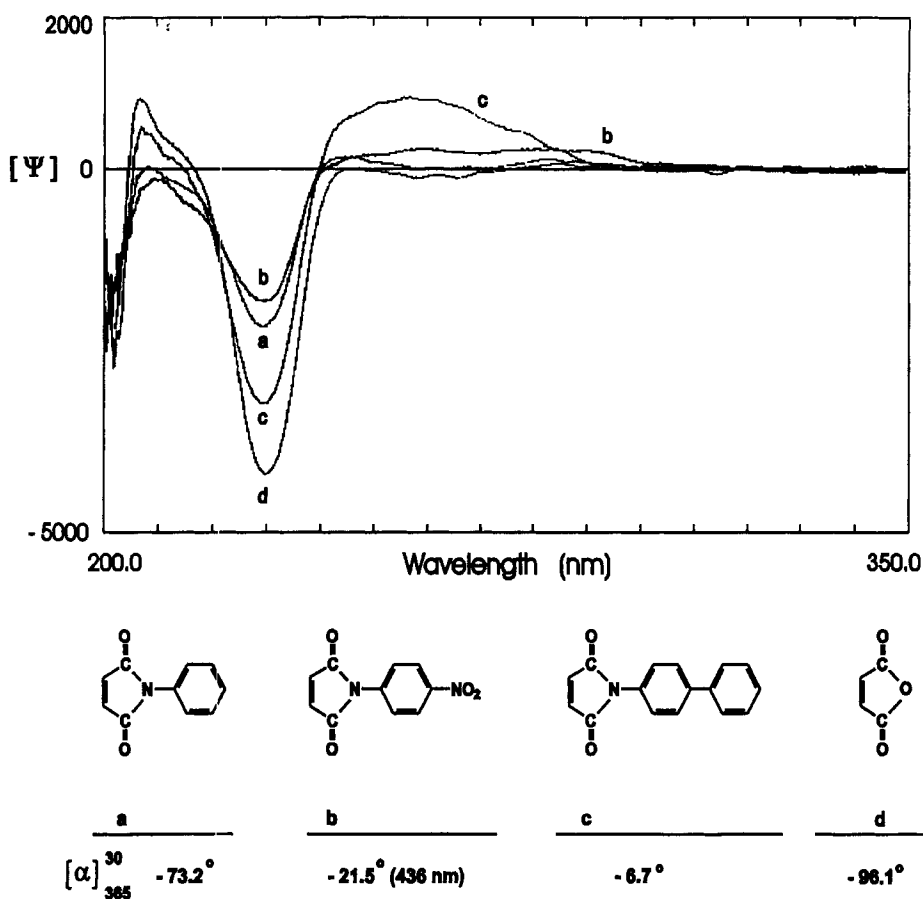
**Figure 11-2.** Copolymerization diagram of **M1** with *N*-phenyl maleimide (Wulff and Krieger, 1994 a).

Figure 11-2 shows the copolymerization behavior for the mannitol derivative **M1** with *N*-phenylmaleimide.

Different compositions of the comonomeric ratios gave nearly 1 : 1 compositions of comonomers in the polymer. Furthermore, the optical rotations of all these polymers are nearly identical, and, more importantly, we can now polymerize to 100% conversion and obtain the same composition and the same optical activity. In Fig. 11-3 the optical rotation and CD of polymers from different *N*-substituted maleimides are shown. Note the strong negative rotation and the CD of the maleic anhydride copolymer.

Copolymers of maleic anhydride can easily be transformed into a variety of other interesting, optically active, functional copolymers. Thus it was possible to react **P4** with 1-decanol and to obtain ester **P5** with strong optical rotation (see Scheme 11-5).

It should be kept in mind that, in the case of copolymers with maleic anhydride or ma-



**Figure 11-3.** Circular dichroism and optical rotation of alternating copolymers of **M1** with substituted maleimides and maleic anhydride (Wulff and Krieger, 1994 a).

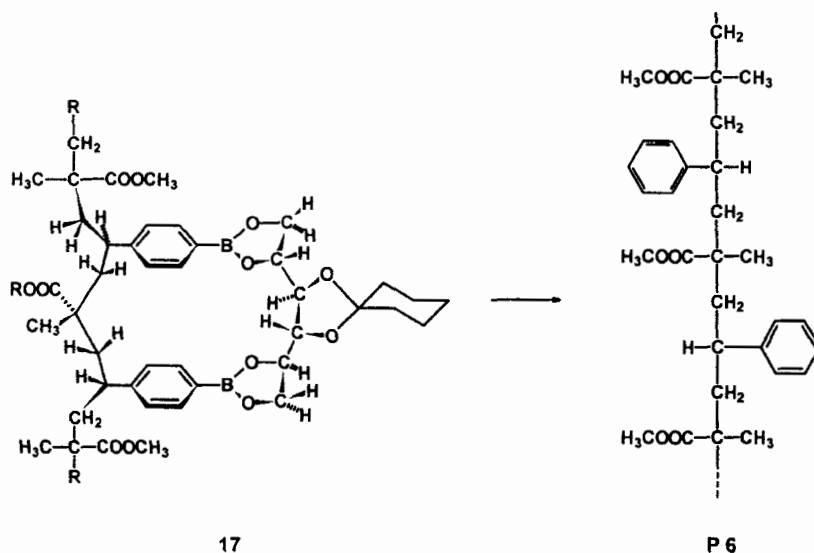
leimides (**P3**, **P4**), the triads contain four stereogenic centers instead of two, as in the case of **P1**. The present investigations show that the chiroptical properties of the polymers are essentially governed by the stereogenic centers of the (*S,S*) dyads. It remains uncertain at present whether there is an asymmetric induction during polymerization on the stereocenters of the maleic anhydride or maleimide unit.

When a similar alternating structure with MMA as the comonomer is envisaged, polymerization conditions known to produce alternating copolymers of MMA and styrene have to be used (see, e.g., Rogueda et al.,

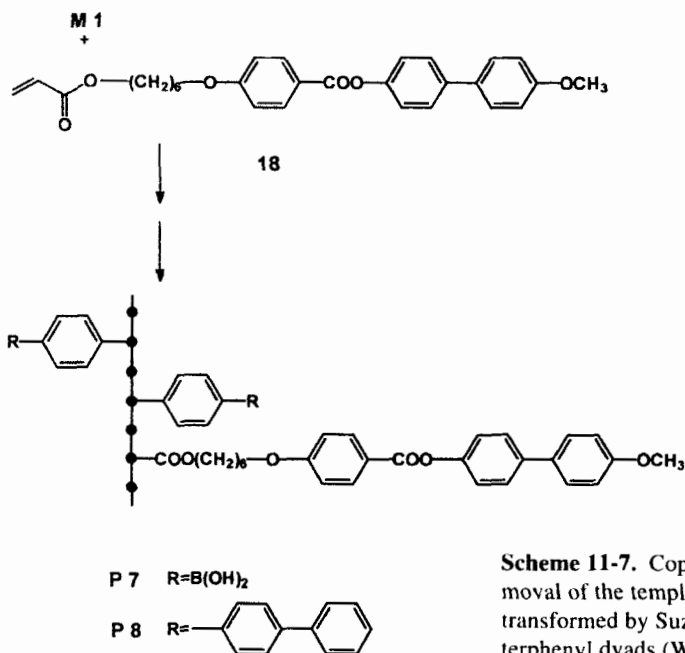
1989). However, copolymerization of **M1** and MMA in the presence of  $\text{AlEt}_{1.5}\text{Cl}_{1.5}$  does not yield the desired structure. Instead, it gives a 21-membered ring **17** owing to insertion of an MMA monomeric unit between the two double bonds of **M1** (see Scheme 11-6) (Wulff and Krieger, 1994 b). The reaction, after removal of the template and the boronic acid, results in mostly alternating styrene-MMA copolymers **P6**. In such a case, much lower optical activity is expected and observed.

The availability of optically active polymers with main chain chirality inspired us to prepare side chain liquid-crystalline poly-





**Scheme 11-6.** Formation of a polymer with 21-membered rings (**17**) on copolymerization of **M1** with methyl methacrylate in the presence of aluminum sesquichloride. Alternating copolymers **P6** are formed after removal of the template.



**Scheme 11-7.** Copolymerization of **M1** with **18** and removal of the template. The phenylboronic acid dyads were transformed by Suzuki reaction with 4-bromo biphenyl to terphenyl dyads (Wulff et al., 1994 a).

mers and to investigate the possible chirality transfer from the main chain to the liquid-crystalline phase (Wulff et al., 1994 a). For this, monomer **M1** was copolymerized

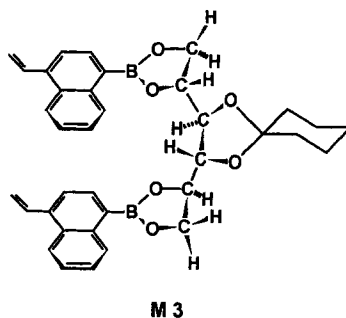
with comonomers carrying mesogenic groups such as **18** (Scheme 11-7). After splitting off the template, polymer **P7** was obtained. This polymer proved, after re-

removal of the boron, to be nematic, and CD measurements in solution revealed that the chromophore of the mesogen showed no Cotton effect. Elongation of the chiral dyad of polymer **P7** by the Suzuki reaction led to polymer **P8**, which possessed terphenyl groups in the chiral dyad. This polymer was liquid crystalline with a cholesteric texture. No chirality transfer to the mesogenic chromophore was observed in solution according to CD, but films of polymer **P8** showed a strong exciton couplet. Therefore only in the liquid-crystalline phase is a special chirality transfer possible through space.

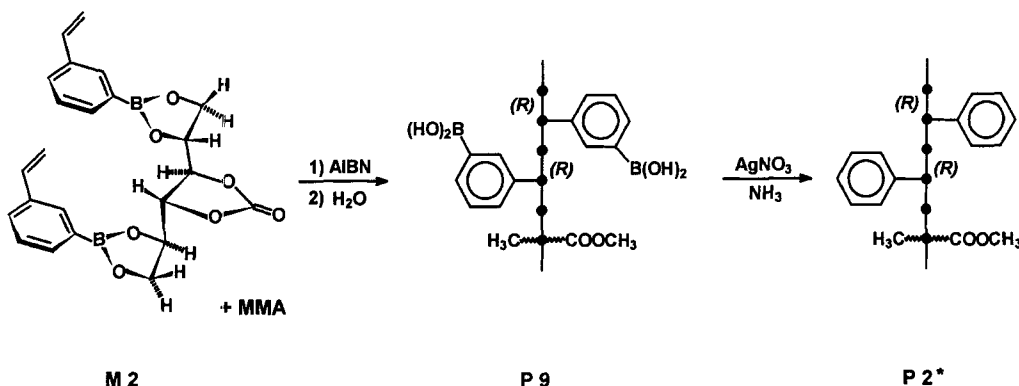
### 11.3.2 Other Types of Template Monomer

Symmetry properties within the monomer will differ distinctly if a meta-substituted compound [in monomer **M2** (Scheme 11-8)] is used instead of the para-vinyl derivatives in **M1** (Wulff and Gladow, 1995). In this case, different conformations originate from rotation around the B–C bond. The standard copolymerization of **M2** with MMA, removal of the template, and deboronation afford the same type of structure as in the case of the para-substituted com-

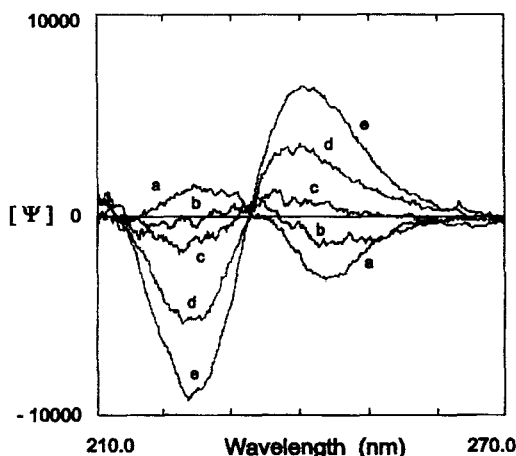
pound **M1** (see Schemes 11-8 and 11-3). However, the chiroptical properties (optical rotation and CD) are of opposite sign. This means that the distyryl dyad predominantly possesses (*R,R*) configuration. Thus it is possible to prepare both enantiomers of the polymers discussed here. The same polymer with (*R,R*) dyads is obtained when in **M1** the L-mannitol derivative is used instead of the D-mannitol derivative (Wulff and Hohn, 1982). We now have two different possibilities in hand to prepare the optical antipodes of the chiral polymers with (*S,S*) dyads.



The nonequivalence of different rotamers in naphthyl derivative **M3** is even more pronounced (Wulff et al., 1995). What is more, restricted rotation might occur in this case. In addition, we have a different chromo-

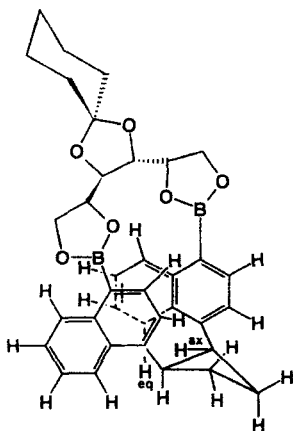


**Scheme 11-8.** Copolymerization of **M2** with methyl methacrylate and removal of the template yields polymer **P9** ( $[\alpha]_{365}^{30} = +31^\circ$ ). Deboronation yields polymer **P1b\*** which is an enantiomer to **P1b** (**P1b\***:  $[\alpha]_{365}^{30} = +29^\circ$ ; **P1b**:  $[\alpha]_{365}^{30} = -25^\circ$ ) (Wulff and Gladow, 1995).



**Figure 11-4.** Dependence of the circular dichroism of **M3** on the recording rate. Curves (a) and (b) represent measuring starting at 270 nm, (c), (d), and (e) starting at 350 nm (downwards). Recording rate 5 nm/min in (b) and (d), 10 nm/min in the case of (c), and 2 nm/min in the case of (e) Wulff et al., 1994b).

phore with absorptions at a  $\lambda$  of 225 nm ( $\epsilon=100\,000$ ), 290 nm ( $\epsilon=5800$ ), and 310–340 nm ( $\epsilon=200$ ). This monomer **M3** shows unexpected behavior. During CD measurements it undergoes an intramolecular [2+2] cycloaddition yielding a cyclobutane derivative (see Fig. 11-4) (Wulff et al., 1994b). The pure cycloadduct **19** can be obtained by prolonged irradiation at 320 nm.

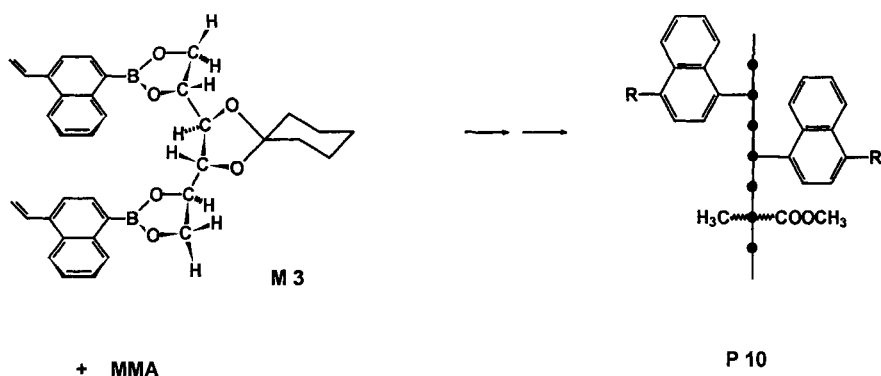


**19**

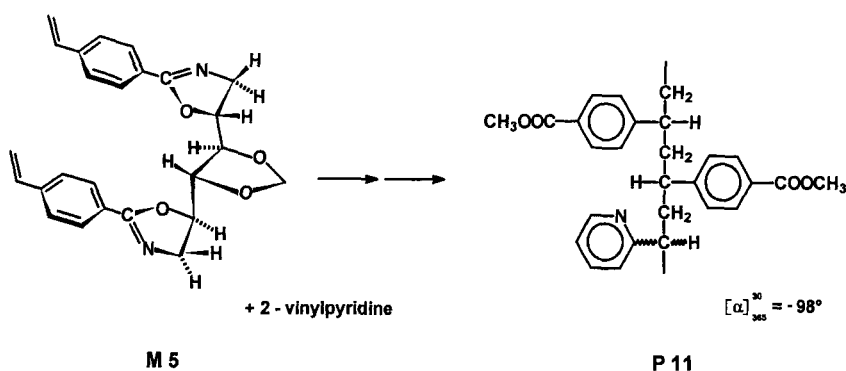
It shows an extremely strong exciton coupling in CD with a  $[\Theta]$  of  $-3 \times 10^5$  at 224.3 nm, and of  $+2.7 \times 10^5$  at 240.8 nm. Since the starting compound **M3** shows almost no CD, this system might provide a very sensitive method for information storage, in which light of a defined wavelength can be detected very sensitively by analyzing the CD of the cyclization product (Wulff et al., 1994b).

Monomer **M3** undergoes a typical asymmetric cyclocopolymerization, for example, with MMA (see Scheme 11-9). After removal of the template, polymer **P10** also shows an extremely intense exciton coupling in CD as does compound **19**. From this fact and application of the exciton chirality rule, the absolute configuration (*S,S*) as well as the conformation of polymer **P10** can be deduced. The ratio of the dyads and the enantiomeric excess is similar to that for the polymerization of **M1** (Wulff and Kühneweg, 1996). Very high optical activity can be obtained using monomer **M4** containing 2-vinyl-naphthyl-1-boronic esters (Wulff et al., 1995). Though these polymers have opposite optical rotation compared to those from 4-vinyl-naphthyl derivatives, the same absolute configuration in the chiral dyad is responsible for optical rotation.

The new monomer **M5** was prepared; this is not only more stable than **M1**, but can also be polymerized by anionic initiation (Wulff et al., 1994c). In order to achieve this, an oxazoline ring was chosen instead of a boronic ester for the connection between template and monomeric unit. The stereochemical properties of an oxazoline ring are very similar to those of the boronic ester. An almost planar five-membered ring is present in both cases. Monomer **M5** can be copolymerized with 2-vinylpyridine by radical as well as anionic initiation. After removal of the template and reesterification, copolymers with high optical activity are obtained



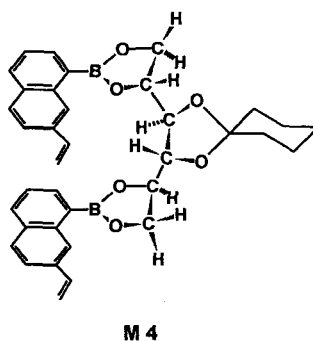
**Scheme 11-9.** Copolymerization of **M3** with methyl methacrylate and removal of the template yields **P10** [ $R=B(OH)_2$  or  $R=H$ ] (Wulff *et al.*, 1995).



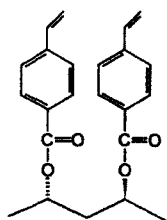
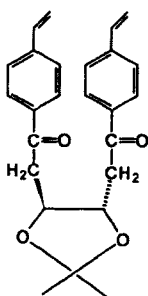
**Scheme 11-10.** Copolymerization of **M5** with 2-vinylpyridine and removal of the template yields **P11** (Wulff *et al.*, 1996).

(see Scheme 11-10). The properties of the copolymers prepared by different types of initiation did not vary significantly. The circular dichroism (CD) of the ester polymers exhibited a strong negative exciton couplet, showing that, according to Nakanishi's exciton chirality rules (Nakanishi and Berova, 1994), the configuration of the dyads is predominantly (*S,S*).

Copolymers with identical dyads as in **P11** (prepared by using template molecules like **M6** and **M7** containing ester connections between template and monomeric units instead of oxazolines) have been reported by Kakuchi *et al.* (1995, 1996a, b, c).



This type of asymmetric cyclopolymerization using ester connections has been systematically investigated by the group of Kakuchi and Yokota [see review, Yokota *et al.* (1995)]. For example, 2,3-*O*-isopro-

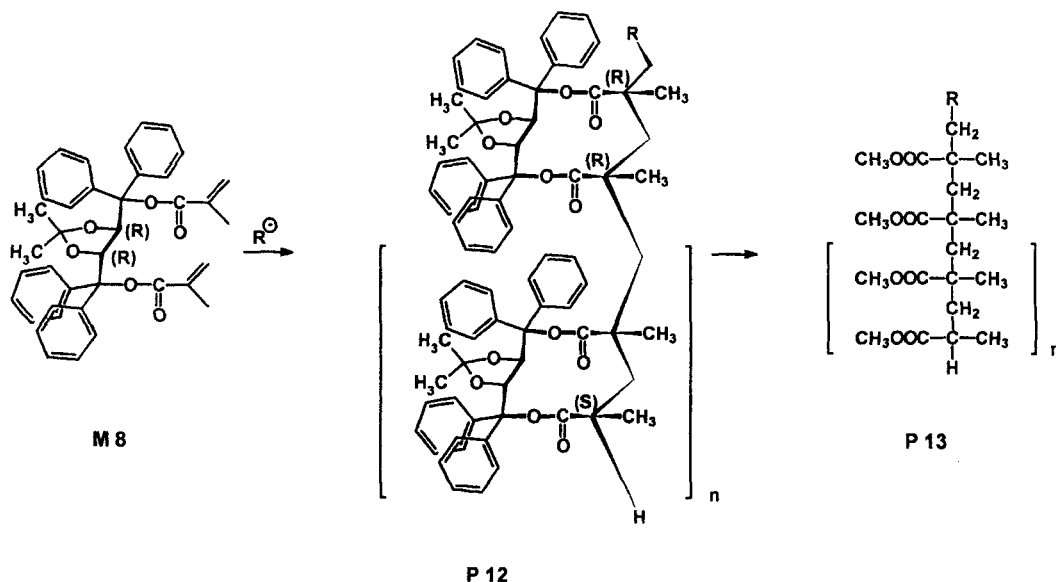
**M 6****M 7**

pylidene-D-threitol-1,4-bis(4-vinylbenzoate) (**M7**) and the 1,4-dimethacrylate as well as (2*S*,3*S*)-2,3-butanediyl-bis(4-vinylbenzoate) (**M6**) and (2*S*,4*S*)-2,4-pentanediy-bis(4-vinylbenzoate) have been copolymerized with styrene. After removal of the template, a poly[(4-vinylbenzoic acid)-*co*-styrene] and a poly[(methacrylic acid)-*co*-styrene], respectively, were obtained (Yokota et al., 1992; Kakuchi et al., 1995, 1996 a, b). Other template molecules used were 1,2,5,6-diisopropylidene D-mannitol and methyl 4,6-isopropylidene-D-glucopyra-

nosid (Haba et al., 1995). In all these cases the copolymers exhibited significant optical activity, although the absolute values of the specific rotation are relatively small compared to those of polymers prepared from **M1** or **M2**. It seems that a higher amount of meso-dyads is produced with monomers like **M6** and **M7**.

Using a very similar but sterically much more demanding template such as the TAD-DOL dimethacrylate **M8** (see Scheme 11-11) produced only meso-dyads on copolymerization with styrene (Wulff et al., 1994 c and 1996). The resulting polymer does not exhibit any optical activity (for homopolymerization of **M8** see Sec. 11-4). CD spectroscopic investigations on copolymers of, e.g., **M6** and **M7** have been performed applying the exciton coupling method of Nakanishi (Nakanishi and Berova, 1994) to elucidate absolute configuration of the polymers (Yokota et al., 1995).

It has long been known that copolymers of 1,2-disubstituted olefins with 1-olefins are chiral and can be obtained optically ac-



**Scheme 11-11.** Anionic homopolymerization of TADDOL dimethacrylate **M8** yields **P12** and, after removal of the template, isotactic PMMA **P13** (Wulff et al., 1994 c. 1996).

tive by asymmetric induction using the template approach (Beredjick and Schuerch, 1958). In this case, the configuration at the 1,2-disubstituted monomeric unit in the main chain determines the chirality. Recently, De et al. (1992) studied the copolymerization of maleimides and indene with styrene derivatives carrying easily removable chiral side chains. After removal of the chiral template, optically active copolymers with relatively low optical rotation were obtained.

## 11.4 Syntheses of Optically Active Homopolymers

Optically active homopolymers are more difficult to obtain than copolymers. In some very special cases it was possible to use chiral catalysts for the polymerization reaction. This has long been tried, but in case of monovinyl compounds only optically active oligomers of propylene could be obtained by Pino et al. (1987). More recently, Coates and Waymouth (1991) succeeded in an asymmetric cyclopolymerization of 1,5-hexadiene. Polymer **P14** was obtained with high optical activity by coordinative polymerization in the presence of (*S*)-ethylenebis-(tetrahydroindenyl)zirconium(*S*)-binaphtholate together with methylaluminumoxane. The stereoisomer shown is the main isomer.

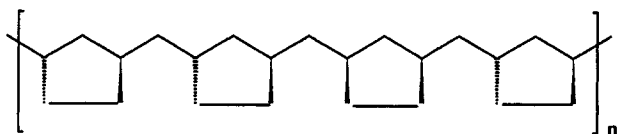
Haba et al. (1993) homopolymerized the divinyl acetal of benzaldehyde with cationic initiation using  $\text{ZnCl}_2/(+)\text{-camphorsulfonic acid}$ . The corresponding polymers had relatively low molecular weight

(2000–2500 g/mol), but a noticeable optical rotation of  $[\alpha]_{435} = -17.1^\circ$ . In this case the stereoisomer causing optical rotation possessed (*S,S*) configuration, as was shown by the synthesis of model compounds.

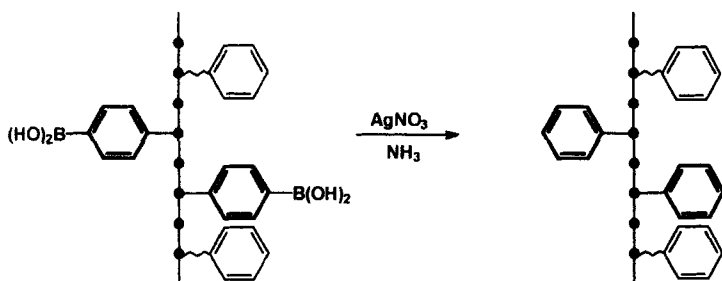
Whereas many examples of chiral copolymers and helical atropisomeric polymers are already known, much less is known on the structural chirality of homopolymers without attached cycles to the main chain. One route to prepare optically active homopolymers with main chain chirality uses the preparation of a heterotactic polymeric chain in which chiral dyads of defined absolute configuration [(*S,S*) or (*R,R*)] alternate with atactic sequences of the same monomeric unit (Wulff and Dhal, 1989). This type of polymer can, e.g., be prepared by copolymerization of **M1** with styrene, followed by removal of the template to give **P15** (see Scheme 11-12). Deboronation yields the homopolymer **P16** with significant optical activity. This was the first time that an optically active vinyl homopolymer (in this case polystyrene) was obtained.

Another stereochemically interesting case is illustrated by isotactic homopolymers of type **21** in which  $\text{R}^1\text{CH}_2$  and  $\text{R}^2$  are different. Unlike **20**, the resulting polymer becomes chiral. It is usually assumed that with polymeric chains the difference of the end groups can be neglected, so that even in the case of a single enantiomer no chiroptical properties will be measurable.

In analogous cases (Mislow and Bickhart, 1977), such behavior has been called cryptochiral. As a result of new preparative methods, it has now become possible to prepare single enantiomers of isotactic chains



**P 14**



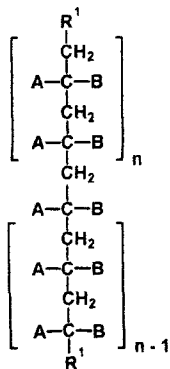
P 15

P 16

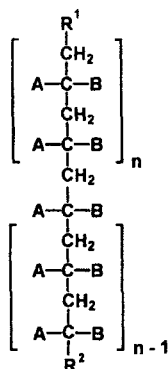
$$[\alpha]_{365}^{30} = -36.0^\circ$$

$$[\alpha]_{365}^{30} = -3.5^\circ$$

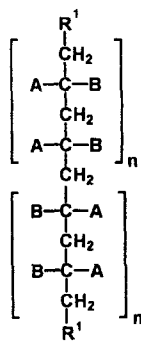
**Scheme 11-12.** Preparation of optically active, heterotactic homopolymers of polystyrene **P16**.



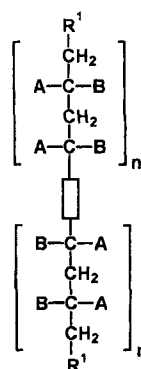
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21



22

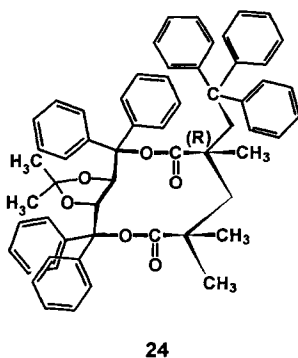


23

of defined chain length, which allow the extent of cryptochirality to be investigated. Anionic polymerization of trityl methacrylate in the presence of chiral catalysts, first introduced by Okamoto and co-workers (Okamoto et al., 1979; Okamoto and Nakano, 1994), gives highly isotactic polymers that exhibit strong optical activity and are present as stable, one-handed (atropisomeric) helices (see Sec. 11-5). After replacement of the trityl group by the much smaller methyl group, the polymer adopts a random-coil conformation and its optical activity becomes very small. Investigations of the oligomers obtained in this polymeriza-

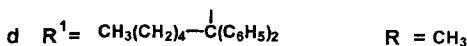
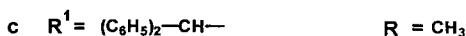
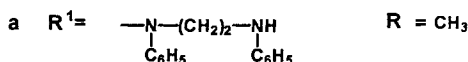
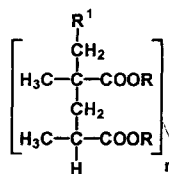
tion reaction (Wulff et al., 1986, 1988; Okamoto et al., 1987b; Nakano et al., 1992), however, show that the stereogenic centers in the main chain are formed with high asymmetric induction and with uniform absolute configuration. Anionic polymerization therefore offers the possibility for the preparation of defined single enantiomers of isotactic PMMA.

Another possibility for the synthesis of single enantiomers of isotactic PMMA was found recently (Wulff et al., 1994c and 1996). The anionic polymerization of the TADDOL dimethacrylate **M8** results in a diastereoselective cyclopolymerization yield-



ing isotactic chains **P12** (see Scheme 11-11). It was shown that cyclization with sterically demanding anionic initiators, yielding the terminated analog of the monocycle **24**, produced with high diastereoselectivity of one diastereoisomer. An 11-membered ring is formed in this case. Anionic homopolymerization leads to the formation of meso-dyads only. Therefore, after removal of the template, a highly isotactic polymer **P13** is obtained in which all chains start with the same absolute configuration. Thus it is possible to prepare chiral and optically active isotactic PMMA if the end groups are not identical. In contrast to the asymmetric polymerization of trityl methacrylate, this leads to an already high enantiomeric excess in the oligomeric state. Isotactic polymers from **M8** without investigating optical activity have also been described by Sogah et al. (1996) and Nakano et al. (1995).

Our attempts to prepare enantiomerically pure or enriched isotactic PMMA **P17** via the trityl methacrylate route (Wulff and Petzoldt, 1991; Wulff et al., 1996) showed that optical activity increases as the difference of the end groups becomes more pronounced, and decreases with higher chain length. The optical activity is much stronger if the enantiomerically pure, isotactic PMMA is forced into a helical conformation by the formation of a stereo-complex with syndiotactic PMMA. Fig. 11-5 a shows

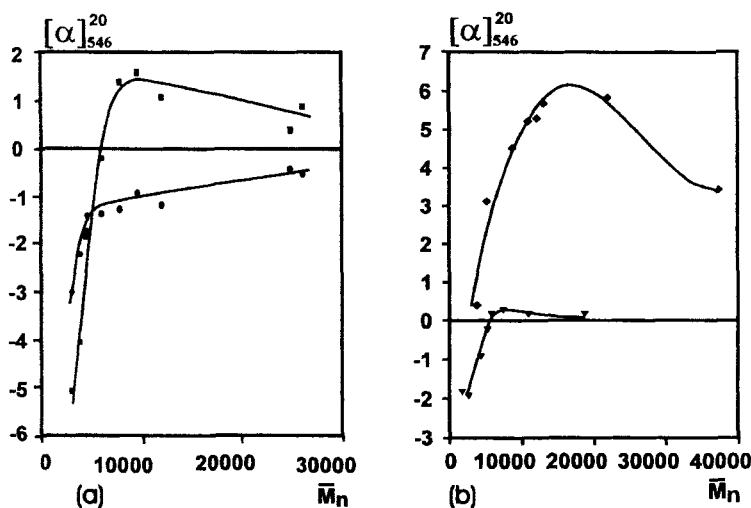


Compounds are prepared from  $R = \text{Trityl}$

that the obtained PMMAs **P17a** show optical rotations  $[\alpha]_{546}^{20}$  from  $-3.0^\circ$  to  $-0.5^\circ$  in the range of molecular weights  $M_n$  3050–26 050 g/mol. Stereocomplexing of these isotactic PMMAs with achiral syndiotactic PMMA ( $M_n = 35\,000$  g/mol) resulted in enhanced optical rotations. Depending on  $M_n$ , the stereocomplexes show a negative optical rotation at lower molar masses, whereas at higher molar masses a positive optical rotation is observed (see Fig. 11-5 a). These values indicate that cryptochirality in isotactic PMMA (and similarly in other polymers) exists only at relatively high molecular weights. It may be expected that only above a  $P_n$  of 500 will chiroptical properties disappear, i.e., the difference of the chain ends can then be neglected.

In our model polymers with isotactic chains such as **20**, the tertiary carbon atoms of the chain can be assigned an absolute configuration in which the substituents are A and B and the two chain ends are of different length. If, for example, the (*R*)-configuration is assigned to carbon atoms of the

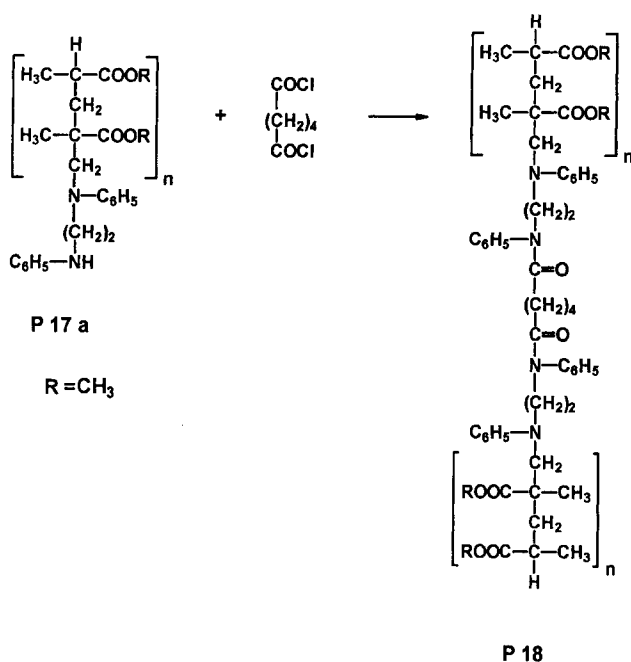




**Figure 11-5.** Optical rotation of isotactic polymers versus the molecular weight: (a) lower curve: isotactic polymers **P17a**; upper curve **P17a** as stereocomplexes; (b) lower curve: isotactic polymers **P17b** as stereocomplexes; upper curve: inverse-diblock isotactic polymers **P18** as stereocomplexes (Wulff et al., 1996).

upper part (e.g., with priority:  $A > B >$  chain ends), then the carbon atoms of the lower half of the chain will have (*S*)-configuration because the chain end, which was previously shorter, now becomes the longer chain. In an isotactic chain like **20**, therefore, one half is (formally) in the (*R*)-configuration and the other in the (*S*)-configuration. It has been pointed out before (Wulff, 1989) that the mirror symmetry of an isotactic chain like **20** can be eliminated if, starting near the middle of the chain, substituents are switched to the opposite side of the chain with respect to the Fischer projection (structural type **22**). The stereogenic centers in the chain now have continuous sequences of either (*R*)- or (*S*)-configuration. Since each section of the chain model is strictly isotactic, we have proposed the description of such structures as “inverse diblock isotactic”. Structure **22** has only a twofold axis of symmetry and is therefore chiral. It is to be expected that with higher molecular weights structure **22** becomes cryptochiral; the upper limit might be considerably higher, as in the case of **21** ( $R^1CH_2 \neq R^2$ ).

As shown before, isotactic poly(methyl methacrylates) **P17** with high enantiomeric purity and varying molar masses are accessible. Polymer type **P17a** still contains a reactive secondary amino group (from the initiator molecule) which is capable of undergoing a coupling reaction. These polymers **P17a** can indeed be coupled to adipoyl chloride in methylene chloride in the presence of triethylamine (see Scheme 11-13) (Wulff et al., 1996). The reaction proceeds slowly and is finished after about 24 hours. Within experimental error, the molar masses of the resulting polymers **P18** are double those of the starting polymer **P17a**, and the polydispersity indices  $M_w/M_n$  are very similar to those of polymers **P17a**. This definitely shows that the coupling reaction was successful and that polymers of type **23** with  $C_2$ -symmetry have been prepared. These  $C_2$ -symmetrical polymers even show at higher molecular weight a considerable optical rotation that can be enhanced by a factor of 7–8 by the formation of stereocomplexes. Compared to the stereocomplexed isotactic structures of **P17a**, from which

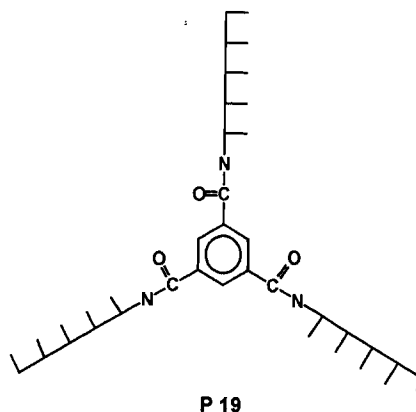


**Scheme 11-13.** Preparation of  $C_2$ -symmetric polymers **P18** by coupling of two isotactic blocks **P17a** to a dicarboxylic acid (Wulff et al., 1996).

they have been prepared, the optical rotation is much higher for polymers **P18**.

Figure 11-5b shows that, even for  $M_n$  values as high as 40 000 g/mol, optical rotations of  $[\alpha]=+3.4^\circ$  still exist. It is clear that at higher  $M_n$  the optical rotation will gradually decrease, but up to  $M_n=100\,000$  g/mol, optical activity can still be expected. At much higher  $M_n$ , no chiroptical properties will be measurable and polymers **P18** will also become cryptochiral.

In a fashion similar to **P18**,  $C_3$ -symmetric star-shaped polymers can be prepared (Wulff et al., 1996). For this, 1,3,5-benzenetricarbonyl chloride is reacted with polymers **P17a**, and polymers **P19** (schematic representation) are obtained after long reaction times. Optical rotations of the three-armed polymers **P19** are somewhat lower than for **P18**, but increase considerably on stereocomplexing. To our knowledge, these are the first examples of  $C_2$ - and  $C_3$ -symmetric polymers from vinyl or vinylidene



monomers with structural chirality in the polymer backbone.

## 11.5 Syntheses of Chiral Atropsiomeric Polymers

In the foregoing Section, it was mentioned that chiral atropsiomeric polymers with a one-handed helix can be synthesized.

This is possible when isotactic polymer chains possess bulky substituents which impose severe steric hindrance. In such a case a one-handed helix can be stabilized, and there is no conformational equilibrium at room temperature or often even at higher temperatures. For every individual chain, only one type of helix occurs. Under usual achiral conditions, the helices will be left- or right-handed and this with equal probability.

Nolte and co-workers (Nolte et al., 1974) were the first to obtain one-handed helices of polyisocyanides [for reviews see, Drenth and Nolte (1979) and Nolte and Drenth (1987)]. Okamoto and co-workers (Okamoto et al., 1979) were successful with poly(trityl methacrylate), and Vogl and co-workers (Corley and Vogl, 1980; Vogl and Jaycox, 1987) obtained polychlorals as optically active polymers with stable, one-screw-sense helices derived from achiral monomers. This type of isomerism can be described as atropisomerism, since it is a form of conformational isomerism in which particular isomers are stabilized by rotational hindrance about single bonds.

Since this chapter deals with the synthesis of optically active vinyl and vinylidene polymers, only atropisomeric polymers of the poly(trityl methacrylate) type will be discussed here.

A predominance of one helical screw sense in poly(trityl methacrylate) and similar polymers can be obtained by one of the following methods:

- (1) By resolution of an equimolar mixture of right- and left-handed helices with the aid of chiral adsorbents (Okamoto et al., 1981 a, 1989; Nakano et al., 1996 a).
- (2) By anionic polymerization of trityl methacrylate using an achiral initiator as well as an optically active chelating agent (Okamoto et al., 1979).
- (3) By anionic polymerization using an optically active initiator and an achiral chelating agent (Okamoto et al., 1980; Wulff et al., 1988).
- (4) Helical polymers with one-handed helical structure can also be obtained by anionic polymerization if the trityl propeller consists of three different “blades” or an otherwise optically active structural unit (Okamoto et al., 1991 a).
- (5) In some cases, radical initiation in the presence of optically active factors also provides one-sense helical polymers (Okamoto and Nakano, 1996).

Poly(trityl methacrylates) or similar polymers are thus obtained with high optical activity. If the bulky substituents (e.g., trityl groups) are removed and replaced by methyl groups, highly isotactic poly(methyl methacrylates) are obtained. The helical conformation is then lost and a random coil conformation is adopted. The optical activity is greatly reduced (see Sec. 11-4) and is only due to configurational chirality, e.g., the difference between the two end groups of the isotactic chain (Wulff and Petzoldt, 1991; Wulff et al., 1996).

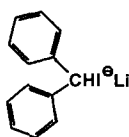
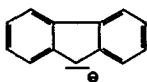
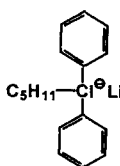
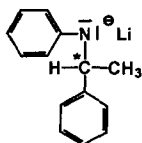
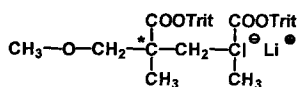
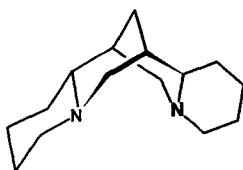
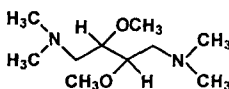
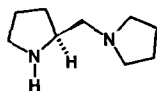
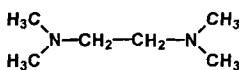
### 11.5.1 Resolution of Polymer Racemates

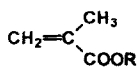
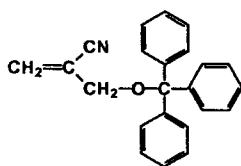
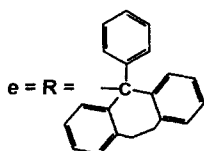
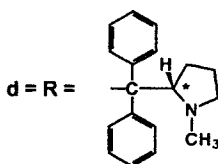
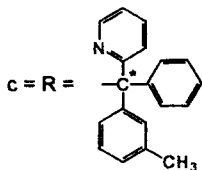
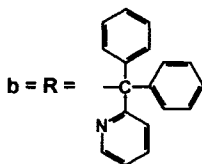
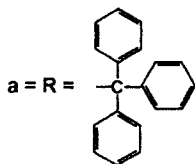
Okamoto et al. (1981 a) separated, e.g., soluble poly(trityl methacrylate) obtained with low optical activity on one-handed helical, insoluble (+)poly(trityl methacrylate) and obtained a positively and a negatively rotating polymer which showed high optical activity. This clearly demonstrates that the helices are growing with almost no helix reversals and are stable under the separation conditions.

### 11.5.2 Anionic Polymerization with Chiral Chelating Agents

Most frequently, helix-sense-selective polymerizations are performed by anionic polymerization in nonpolar solvents such as toluene and at low temperature (e.g.,  $-78^{\circ}\text{C}$ ) (see Okamoto and Nakano, 1994). Achiral initiators, e.g., **25**, **26**, or **27**, are

used together with an optically active chelating agent such as **30**, **31**, or **32**. Most interesting are the DDB (**31**) initiators which are derived from tartaric acid and can easily be obtained as (*S,S*) and (*R,R*) forms. Some monomers give higher enantioselectivity with (+)PMP (**32**) (obtained from L-proline). Typical monomers include trityl methacrylate **M9a** and diphenyl-2-pyridylmethyl

**25****26****27****28****29****(-)-Sparteine****30****DDB****31****PMP****32****TMEDA****33**

**M 9****M 10**

methacrylate **M9b**. The advantage of the latter, though more difficult to prepare, is that the amount of oligomers formed during the polymerization is much lower than with trityl methacrylate.

With trityl methacrylate, half of the initiator molecules remain in the form of oligomers. These oligomers are a mixture of diastereoisomers, which for steric reasons do not propagate further and can be isolated and elucidated in their structure (Wulff et al., 1986; Okamoto et al., 1987b). A detailed investigation with different initiator systems and an analysis of the diastereomeric as well as the enantiomeric composition

of the oligomers with  $P_n$  1–8 was performed by Okamoto's group (Nakano et al., 1992). From all these investigations, it became clear that the first steps of polymerization are not highly diastereoselective. Only the isotactic chains propagate to higher polymers. After the formation of the octamer, monomer addition becomes much faster and is highly stereoselective due to a helix control mechanism. At a  $P_n$  = 7–9 probably two turns of the helix are finished.

Optically active (one-handed helical) poly(trityl methacrylate) has been given special attention, since it can be used as a chromatographic support for racemic resolution. Chromatographic columns filled with poly(trityl methacrylate) supported on silica gel are now commercially available (Okamoto et al., 1981b). A drawback of these materials is their chemical instability during prolonged use. Owing to fission of the trityl groups, the helicity is destroyed and the ability for racemic resolution is lost. For this reason, new poly(triarylmethyl methacrylates) with better hydrolytic stability were investigated (Okamoto and Nakano, 1994). Another interesting example is monomer **M9e** (Nakano et al., 1996b), which affords a very stable, one-handed helical polymer. A very stable chiral polymer is also formed from  $\alpha$ -(trityloxymethyl)acrylonitrile **M10**, which belongs to a different structural type (Wulff and Wu, 1990a). The structural requirements for monomers to form a stable one-handed helix have been investigated further (Wulff and Wu, 1990b; Okamoto and Nakano, 1994).

### 11.5.3 Anionic Polymerization with a Chiral Initiator

The stereochemical regulation of the chain growth up to  $P_n$  = 8 is mainly governed by two factors: (1) a chelate control of the optically active chelating agent and (2) a

backbone control of the stereogenic centers of the growing macroanion. Okamoto et al. (1980) used the optically active initiator **28** together with the achiral chelating agent TMEDA **33** for the polymerization of trityl methacrylate. They obtained polymers with optical activities of around 17–30% compared to those poly(trityl methacrylates) which have been prepared with optically active chelating agents.

In order to get a better picture of the backbone control we prepared optically active dimers **29** with (R) and (S) configurations, which are very similar to the end groups of the macroanion (Wulff et al., 1988; Vogt and Wulff, 1989). With these initiators and TMEDA, the optical activities are higher (~50%) than with **28**, but compared to optically active chelating agents the backbone control is apparently less efficient. This is further demonstrated by the addition of optically active chelating agents such as (+) or (–) DDB. Regardless of the chirality of the initiator, the chelating agents completely determine the helix sense and the optical activity of the polymers. Thus the backbone control is overruled by the chirality of the chelating agent.

#### 11.5.4 Anionic Polymerization of Monomers with Chiral Propellers

If methacrylates with an optically active propeller like **M9c** or **M9d** are polymerized, the chirality of the propeller induces a helix-sense-selective polymerization. In this case, no chiral initiator or chelating agent has to be added. These helical polymers exhibit some very interesting special features. If (+)**M9c** is polymerized in the presence of TMEDA, a polymer with  $[\alpha]_{365}^{25} = +262^\circ$  is obtained. In the presence of (+)DDB, the rotation of the resulting polymer is  $[\alpha]_{365}^{25} = +1125^\circ$ , and in the presence of

(–)DDB  $[\alpha]_{365}^{25} = -845^\circ$  (Okamoto et al., 1991a). These results show that the chiral chelating agents have a much stronger influence on the helix-sense-selective polymerization than the propeller, and control the formation of the helix sense. After treatment of these three polymers at 60 °C for some time, a mutarotation occurs, resulting for all three polymers in nearly the same optical rotation of  $[\alpha]_{365}^{25} = +1370^\circ$  to  $+1646^\circ$ . The helicity seems to have become the same in all three cases under the influence of the chirality of the ester group through a helix-helix transition. This means that the kinetically controlled formation of the helices is replaced by thermodynamic control during a helix-helix transition. In the case of polymers of **M9d**, a reversible helix-helix transition has been observed, depending on the solvent (Okamoto et al., 1991b). Helix-helix reversals have also been reported for optically active polymers from **M9b** (Okamoto et al., 1989).

#### 11.5.5 Helix-Sense Selective Radically Initiated Polymerization

Whereas until now it was not possible to polymerize trityl methacrylate helix-sense-selectively by radical initiation, Okamoto et al. were recently more successful with monomer **M9e** (Okamoto and Nakano, 1996; Nakano et al., 1996a). Helix-sense-selective radical polymerizations were brought about by using optically active initiators, chain-transfer reagents, or a transition metal complex radical species.

### 11.6 Acknowledgement

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## 12 The Synthesis and Characterization of Dendritic Molecules

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## List of Symbols and Abbreviations

$c$	concentration
$d$	diameter
$D$	effective diffusion coefficient
$f_{\text{br}}$	branching factor
$J$	coupling constant
$k_{\text{B}}$	Boltzmann constant
$m$	mass
$m_1$	generation at which full congestion is reached
$M$	molecular weight
$M_{\text{R}}$	molecular mass
$M_{\text{w}}/M_{\text{n}}$	polydispersity
$n$	number
$P$	branch segment length
$R_{\text{H}}$	hydrodynamic radius
$T$	absolute temperature
$T_1$	spin lattice relaxation
$T_2$	relaxation
$T_{\text{g}}$	glass transition temperature
$x$	number, number of benzene units
$y$	number
$z$	charge
$\alpha$	branching efficiency
$\eta$	viscosity at $T$
$[\eta]$	intrinsic viscosity
$\lambda$	wavelength
$\pi$	compression
AFM	atomic force microscopy
ANB	average number of nonlinear branches per nonterminal unit
ATRP	atom transfer radical polymerization
bipy	2,2'-bipyridene, 2,2'-bipyridyl
Bn	benzyl
BOC	<i>tert</i> -butoxycarbonyl
Bu	butyl
c	core
CAD	collision-activated dissociation
CD	circular dichroism
COSY	correlated spectroscopy
D	dendrimer
DAB	diamino butane
DABCO	1,4-diazabicyclo[2,2,2]octane
DB	degree of branching

dba	dibenzylideneacetone
DCC	dicyclohexylcarbodiimide
DEAD	diethylazodicarboxylate
DLS	dynamic light scattering
DMF	dimethylformamide
DOSY	diffusion ordered NMR spectroscopy
DSC	differential scanning calorimetry
ESI-MS	electrospray ionization mass spectrometry
Et	ethyl
FAB	fast atom bombardment
G	generation
GPC	gel permeation chromatography
GTP	group transfer polymerization
1-HBT	1-hydroxybenzotriazole
HMPA	hexamethylphosphoramide
HPLC	high performance liquid chromatography
IR	infrared
LC	liquid-crystal
LDA	lithium di-isopropylamide
LLS	laser light scattering
M	monomer
MALDI-TOF	matrix-assisted laser desorption time-of-flight
Me	methyl
MS	mass spectrometry
MW	molecular weight
NMR	nuclear magnetic resonance
PAD	phenyl acetylene dendrimer
PAM	phenylacetylene macrocycle
PAMAM	polyamidoamine
PEO	polyethylene oxide
Ph	phenyl
PMMA	poly(methylmethacrylate)
PS	polystyrene
QELS	quasi elastic light scattering
RT	room temperature
SCVP	self-condensing vinyl polymerization
SEC	size-exclusion chromatography
<i>t</i> -BOC-L-Phe	<i>t</i> -BOC protected L-phenylalanine
TEA	triethylamine
TEM	transmission electron microscopy
TEMPO	tetramethylpiperidine- <i>N</i> -oxide
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TLC	thin layer chromatography
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine

TMS	trimethylsilyl
Ts	tosyl
TTF	tetrathiafulvalene
UV	ultraviolet
VPO	vapor pressure osmometry
W	wedge

## 12.1 Introduction

The synthesis of molecules with precise dimensions has always been the domain of the organic chemist. The recent progress made in natural product synthesis is fascinating (the complexity of the targeted structures has increased significantly) and is mainly due to advances in synthetic methodologies on one hand and enormous developments in new characterization techniques on the other. In the synthesis of polymers, the progress is equally impressive, as is obvious from the other chapters in this series. However, in contrast to those active in the area of organic chemistry and biochemistry, polymer chemists have accepted that molecular weight distributions are present in high molecular weight materials as synthesized by various polymerization methodologies. These molecular weight distributions are the result of the statistical nature of all polymerization procedures known in polymer chemistry: Even in “living” polymer systems, polymers have a statistical distribution of chain lengths, although the polydispersity can be as low as 1.01.

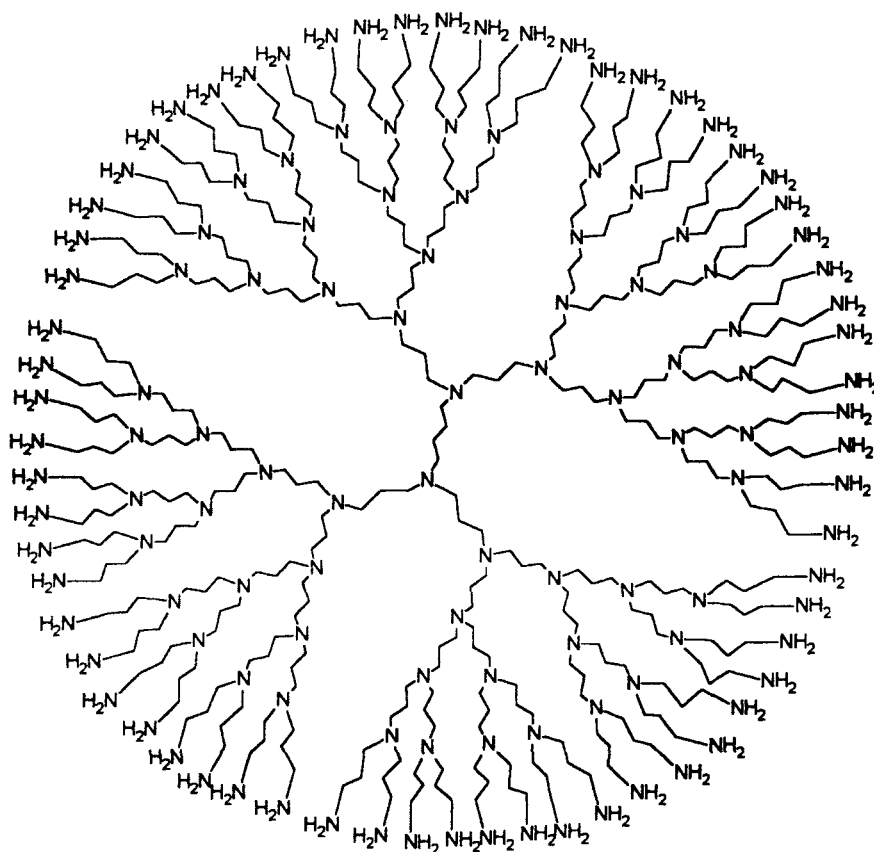
Recently, dendrimers have been introduced as a new class of macromolecules (Newkome et al., 1985; Tomalia et al., 1985, 1986). These types of molecules fit perfectly in the no-man’s-land between organic and polymer chemistry: Dendrimers are macromolecules with a completely defined structure, made by a step-by-step procedure and, in theory, lacking polydispersity (i.e.,  $D=1$ ). The seminal contributions of Newkome (Newkome et al., 1985) and Tomalia (Tomalia et al., 1986) have initiated a tremendous activity in the fields of dendrimer chemistry and chemistry related to other well-defined, highly branched macromolecules. Many intriguing properties of dendrimers have been proposed, and some of them have been disclosed recently. The

supposed properties of dendritic materials are related to their well-defined, three-dimensional architecture and their high number of end groups. These features indicate possibilities for a densely packed surface with cavities present in the dendrimer interior and allow simple modification methods leading to the use of dendritic materials in catalysis, nanotechnology, polymer technology (polymer additives), and biomedical applications (e.g., controlled drug release systems).

Various authors have written excellent books and reviews on dendritic molecules (Newkome et al., 1996; Issberner et al., 1994; Tomalia et al., 1990a; Ardoin and Astruc, 1995; Fréchet et al., 1996; Malmström and Hult, 1997). For details on the many possible applications of dendrimers, the reader is referred to these excellent reviews. Here, we will not attempt to describe all known dendritic molecules, but we will emphasize on the synthetic methodologies that are the basis for the production of dendrimers. Furthermore, the molecular characterization of dendrimers will be stressed. Finally, the structural properties of a selected number of dendrimers will be discussed.

## 12.2 Methodologies in Dendrimer Synthesis

Dendrimers are highly and regularly branched polymers with a layered structure (every layer is a so-called generation). In Fig. 12-1, a fifth generation poly(propylene imine) dendrimer is shown as an example. The architectural features of dendrimers resemble trees and cauliflowers. As a result, trivial names like arborols (*arbor*, Latin = tree), cauliflower polymers, cascade polymers, and molecular fractals have been coined for these macromolecules. Of course, the word dendrimer, which is now



DAB-dendr-(NH<sub>2</sub>)<sub>64</sub>

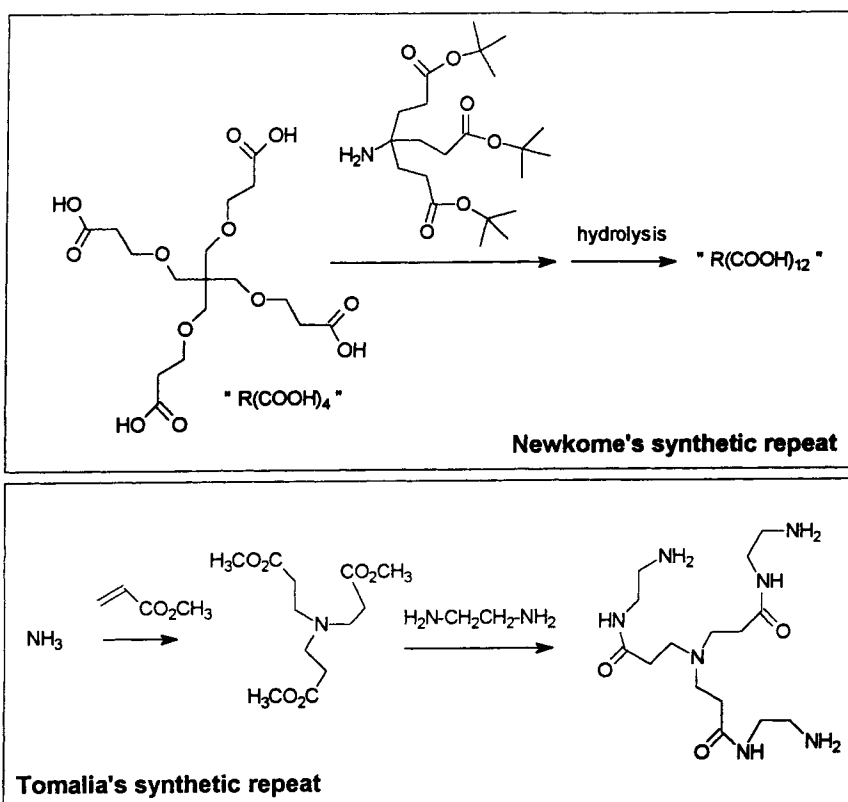
**Figure 12-1.** The fifth generation of the commercially available poly(propylene imine) dendrimers: DAB-dendr-(NH<sub>2</sub>)<sub>64</sub> (de Brabander-van den Berg and Meijer, 1993). DAB is an indication for the diaminobutane core.

used by every author in the field, is also trivial (*dendro*, Greek = tree-like). The current scientific nomenclature rules do not suffice to describe the molecular structure of dendrimers efficiently. Therefore elegant cascade nomenclature rules have been proposed by Newkome et al. (1993 a).

The molecular structure of dendrimers finds its origin in the stepwise synthesis of these structures. The same chemistry and building blocks are used for every new generation. Two completely different synthetic approaches towards dendrimers of higher generations have been introduced: the di-

vergent and the convergent approaches. More recently, combinations of the two have been explored.

The oldest methodology towards dendrimers is the divergent synthesis. Using this approach, the addition of a monomer to a multivalent core molecule is followed by an activation (or deprotection) step resulting in a structure with a multiplied number of end functionalities at the periphery. With every sequence of (generally two) reactions, one generation is added. Independently, Newkome and Tomalia have introduced this strategy to synthesize well-defined dendrit-



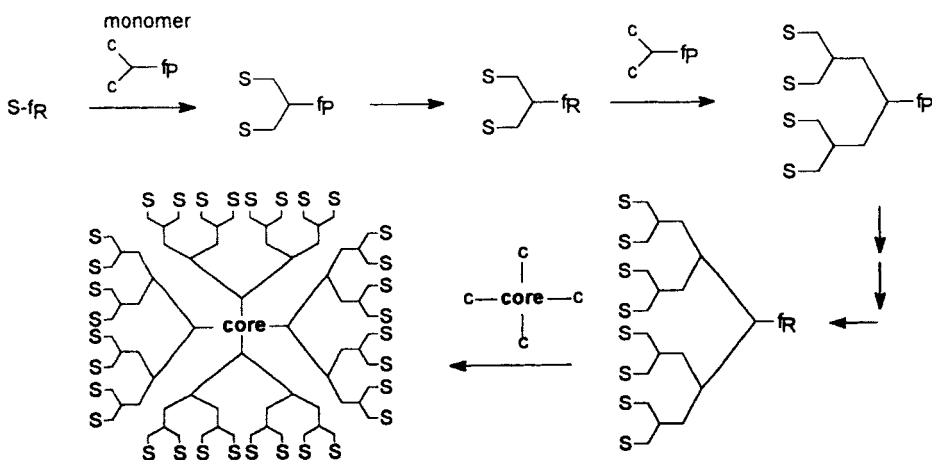
**Figure 12-2.** The divergent approach towards dendrimers. Newkome uses a branched building block and Tomalia uses the chemistry to obtain branched structures.

ic macromolecules of high molecular weight. The divergent dendrimer synthesis is an adaptation of the iterative chemistry leading to cascade molecules as reported on by Vögtle (Buhleier et al., 1978). Within the divergent approach, we can differentiate two slightly different reaction schemes, as illustrated in Fig. 12-2. In one scheme, the branching originates from the building blocks which are branched (used by, e.g., Newkome). In the other scheme, the branching is obtained by the chemistry employed: The double Michael addition of methyl acrylate to a primary amine (used by, e.g., Tomalia). Both reaction schemes will be discussed in detail later.

In both reaction schemes, the number of reaction sites multiplies with every genera-

tion, and it therefore becomes increasingly difficult to achieve full conversion. At a certain generation, the conversion will be controlled by steric circumstances. 100% conversion will not be possible at this point, simply because there is not enough space to accommodate all the new end groups. The conversion will stop at the so-called 'sterically controlled stoichiometry'. However, long before this generation is reached, full conversion will also be problematic. In a divergent dendrimer synthesis, a huge number of reactions have to be performed on the same molecule, meaning that only 100% conversion per reaction will lead to defect-free dendrimers. An average yield of 99.5% per reaction will, in the case of the synthesis of the fifth generation poly(propylene





**Figure 12-3.** The concept of a convergent dendrimer synthesis. Every step involves a wedge with a focal group (f) that is protected ( $f_p$ ) or reactive ( $f_R$ ). An activated wedge reacts with a monomer to afford a dendrimer with a higher generation; a monomer is a molecule with (at least) two coupling sites (c) and a protected focal point. The synthesis begins at the surface (s) and ends at the core.

imine) dendrimer (this molecule needs 248 reactions), only result in  $(0.995^{248}) \times 100 = 29\%$  of defect-free dendrimer. Therefore the divergent synthesis can be referred to as the macromolecular approach to dendrimers, since the presence of a small number of statistical defects cannot be circumvented. Such statistical defects are also well known from Merrifield syntheses of polypeptides and polynucleotides (Solomons, 1996).

In order to overcome the difficulty of the many reactions that have to be performed at the steadily growing number of end groups, Fréchet and co-worker introduced the convergent synthesis of dendrimers (Hawker and Fréchet, 1990). Instead of divergently growing the dendrimer from the core to the periphery, the convergent growth strategy starts from the periphery and ends at the core (see Fig. 12-3). This approach eliminates the exponential increase of reactive sites which is characteristic for divergent synthetic procedures. In fact, the strength of a convergent synthesis is the constant number of reactive sites for the production of every new generation. Thus only a limited num-

ber of side products can be formed, and it is possible to purify every generation by methods well known in organic chemistry (typically, column chromatography and precipitation are used). These purifications are inconceivable for divergently produced dendrimers of higher generations. Therefore the convergent synthesis can be referred to as the organic approach to dendrimers: Products can be purified and will, in general, be defect-free.

Following the above synthetic methodologies, a large variety of dendrimers have been prepared and characterized. We have chosen to highlight a limited number of dendrimers to illustrate the different approaches, chemistries, characterizations, and applications. In our personal selection, we have been led by the idea that those dendrimers that have attracted the attention of a major part of the polymer community are worth mentioning here. Therefore the first part of this chapter will deal with Newkome's arborols, Tomalia's Starburst dendrimers, DSM's poly(propylene imine) dendrimers, Fréchet's polyether dendrim-

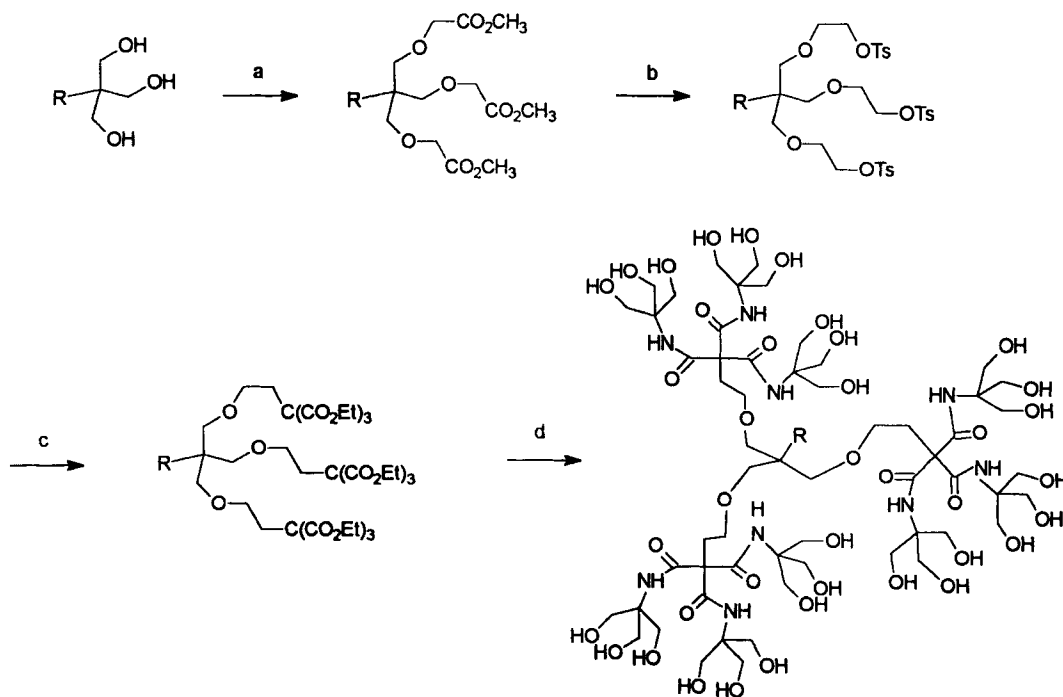
ers, and Moore's phenylacetylene dendrimers. These dendrimers have not only been studied and applied by the original authors, but have also been used and characterized by others. Obviously, our personal selection is limited and does not reflect the importance or beauty of many other dendritic structures with special functions. In the second part of this chapter, we will discuss some new developments in the synthesis and characterization of dendrimers as well as hyperbranched polymers.

## 12.2.1 Divergent Methods

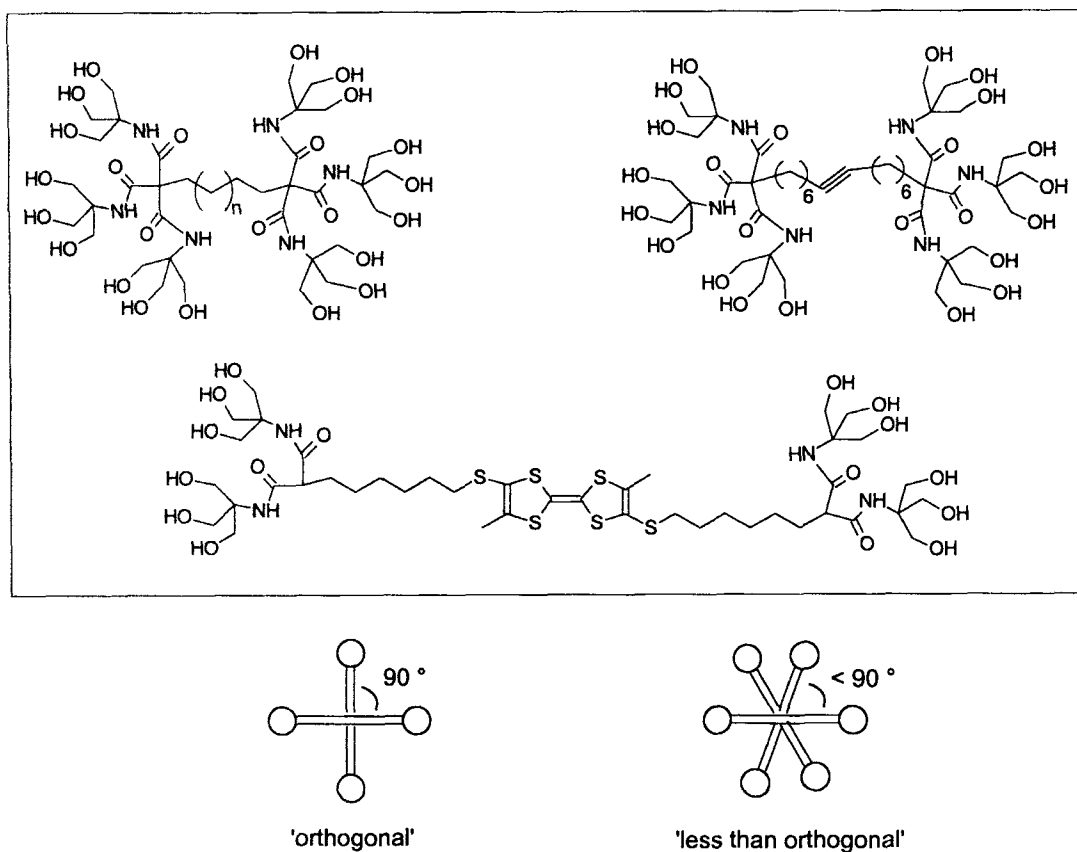
### 12.2.1.1 Newkome's Arborols

In 1985, Newkome presented highly branched, tree-like molecules with terminal alcohol functions, prompting the author to

name these molecules 'arborols' (*arbor*=tree, Latin) (Newkome et al., 1985). The synthetic procedure towards these dendrimers does not rely on an exact iterative process, but uses three different building blocks, each possessing a three-directional ( $1 \rightarrow 3$ ) branching center (see Fig. 12-4). The trifunctional core molecule, 1,1,1-tris(hydroxymethyl)hexane, is extended by reacting the alcohols with chloroacetic acid. After esterification of the carboxylic acids, reduction of the resulting methyl esters, and activation of the three alcohol functions by tosylation, the next branching unit, the sodium salt of triethyl methanetricarboxylate  $[\text{NaC}(\text{CO}_2\text{Et})_3]$ , can be introduced via a Williamson coupling reaction. The final branching molecule, tris(hydroxymethyl)-aminomethane, is simply introduced in an amidation reaction. In addition to this first arborol, structural variations have been re-



**Figure 12-4.** The first reported synthesis of so-called 'arborols' by Newkome: a) 1.  $\text{ClCH}_2\text{COOH}$ ,  $t\text{-BuOK}$ ,  $t\text{-BuOH}$ , 2.  $\text{MeOH}$ ,  $\text{H}^+$ ; b) 1.  $\text{LiAlH}_4$ , 2.  $\text{TsCl}$ , pyridine; c)  $\text{NaC}(\text{CO}_2\text{Et})_3$ ; d)  $\text{H}_2\text{NC}(\text{CH}_2\text{OH})_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{R}=\text{n-alkyl}$ .

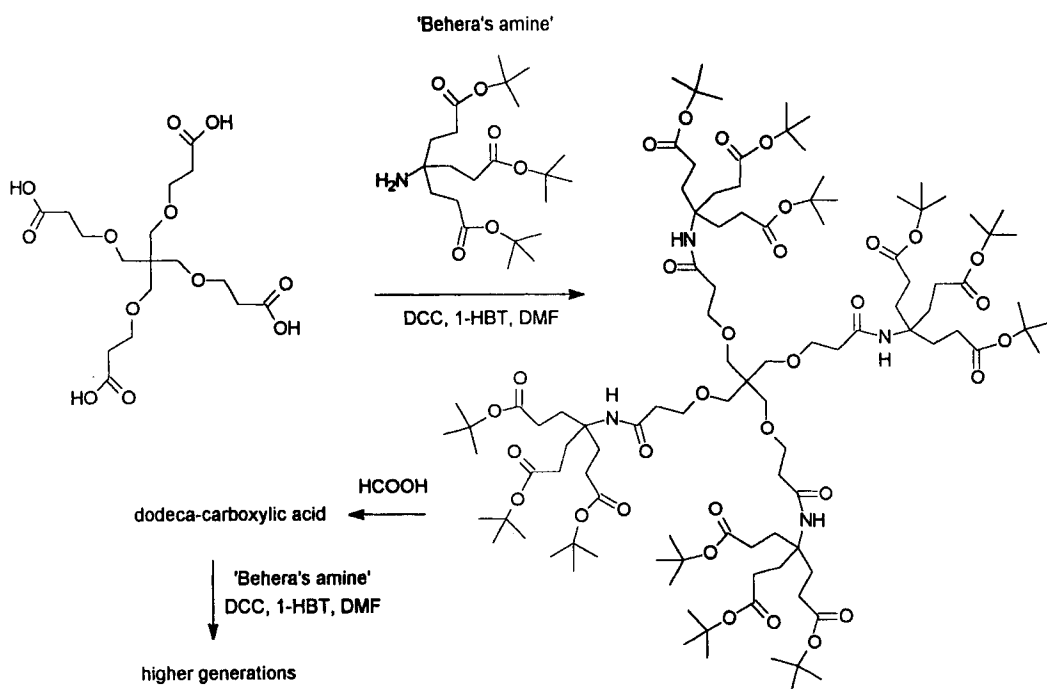


**Figure 12-5.** Three types of 'bola-amphiphiles' with arborol polar head groups and various apolar spacers. Two modes of packing (orthogonal and less-than-orthogonal) of the bola-amphiphile molecules have been proposed. These amphiphiles can schematically be drawn as dumbbell structures.

ported in which other core molecules have been applied; 1,3,5-tris(bromomethyl)benzene (Newkome et al., 1986a) and even calixarenes (Newkome et al., 1991a) have been used effectively as cores.

Based on a similar sequence of reactions, various 'bola-amphiphiles' have been produced. Bola-amphiphiles are molecules bearing two polar end functionalities separated by an apolar (alkyl) spacer (Fuhrop and Mathieu, 1984). These amphiphiles are known to assemble in long rod-like micelles in water, resulting in the formation of aqueous gels. Bola-amphiphiles with varying spacers have been investigated (Fig. 12-5),

showing that not every design gives gel formation in water, i.e., not every spacer has the proper steric parameters to allow a packing process in water. In fact, in the series of amphiphiles with alkyl spacers, only the  $C_{10}$ -derivative forms a gel in water. TEM photographs of this derivative show the presence of linear assemblies with diameters in the order of the length of one molecule (ca. 35 Å) (3.5 nm) (Newkome et al., 1986b). It has been suggested that one  $C_{10}$  alkyl spacer has an extended conformation and is orthogonally stacked on top of another spacer (Fig. 12-5). When an alkyne moiety is introduced in the alkyl spacer, ag-

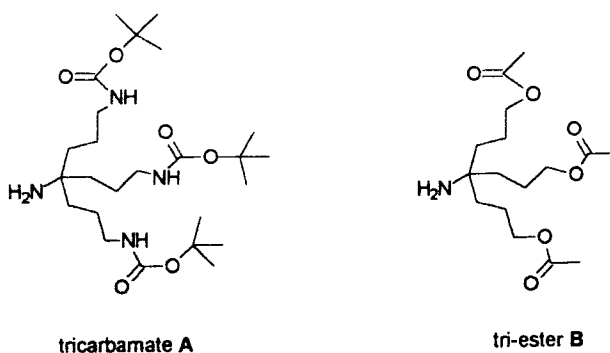


**Figure 12-6.** Newkome's iterative synthetic procedure towards dendrimers with carboxylic acid end functionalities. A repetition of coupling reactions with Behera's amine and deprotections of the *tert*-butyl esters can be used to build up higher generation dendrimers.

gregation of the linear strands to rope-like higher structures is observed (Newkome et al., 1992). The origin of the helical rope structures is sought in a less-than-orthogonal chain alignment of the hydrophobic spacers in the linear strand. String-like higher structures have also been observed for bola-amphiphiles with tetrathiafulvalene (TTF) moieties incorporated in the hydrophobic spacers (Jørgensen et al., 1994). Finally, when spirane or biphenyl hydrophobic spacers are used, the resultant amphiphiles fail to gel in aqueous solutions (Newkome et al., 1993 b).

The tris(hydroxymethyl)aminomethane building block is not suited for an iterative synthesis of higher generation dendrimers, because the neopentyl electrophile centers cannot be used in  $S_N^2$  reactions (March, 1992). A successful building block for such

an iterative procedure has been found in 'Behera's amine' (see Fig. 12-6) (Young et al., 1994; Newkome et al., 1993 c). 'Behera's amine' can be coupled to a four-directional tetra-carboxylic acid core using standard amidation conditions, i.e., conditions also applied in peptide synthesis [dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (1-HBT), dimethylformamide (DMF), 25 °C]. Subsequently, the *tert*-butyl ester masking groups are hydrolyzed under acidic conditions (pure HCOOH) to afford the first generation dendrimer with 12 terminal carboxylic acid functionalities. Repetitive amidation and hydrolysis has produced dendrimers up to generation  $G_5$ ; this is the dendritic material with, ideally, 972 carboxylic acids at the periphery. All dendritic materials with carboxylic acid terminal functionalities have



**Figure 12-7.** Two alternative building blocks for Behera's amine: tricarbamate **A** and tri-ester **B**.

been isolated as white solids, most of which display melting trajectories.

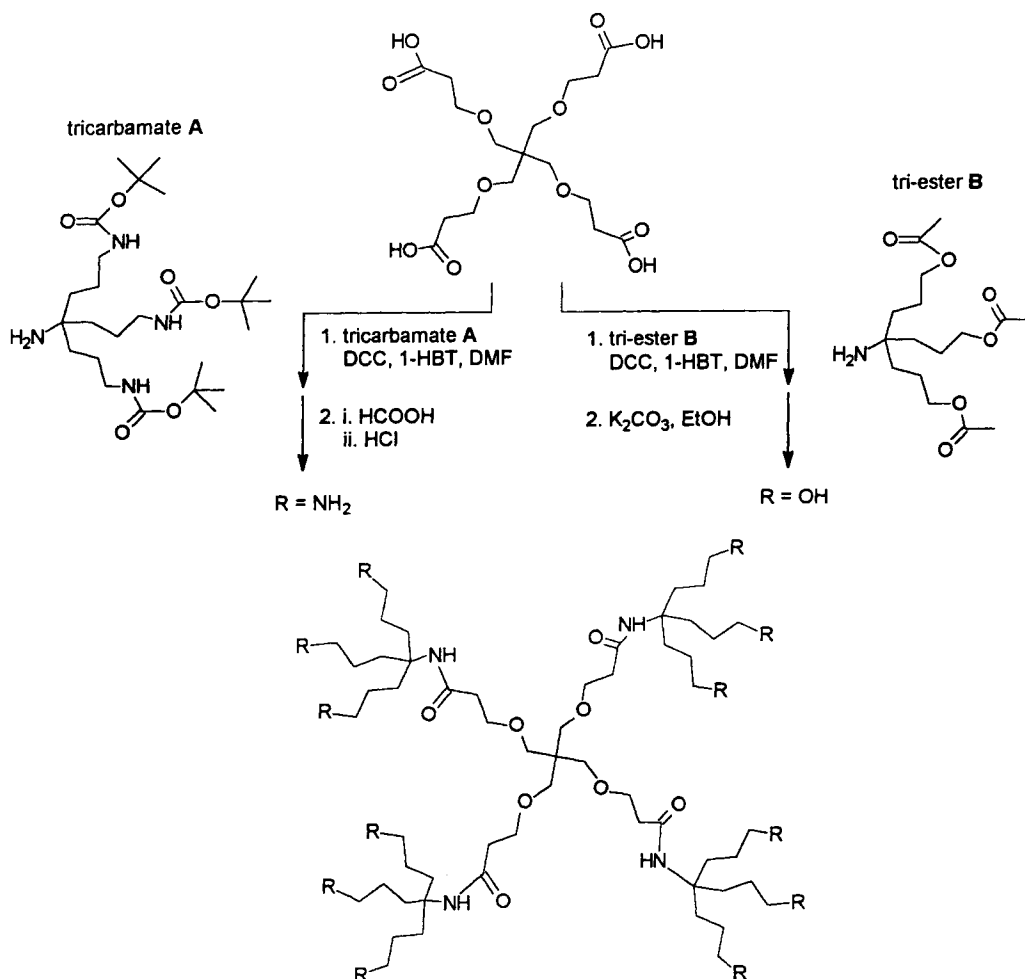
The applied synthetic route to higher generation dendrimers can be modified to generate dendrimers with exterior alcohol or amine functions (Young et al., 1994). For this purpose, two alternative building blocks with 1 → 3 branching points have been synthesized (see Fig. 12-7); both these molecules (the tri-carbamate **A** and the acetyl protected tri-alcohol **B**) originate from nitromethane. In Fig. 12-8, the uses of these two building blocks **A** and **B** are explained.

Dendrimers with amine terminal functionalities can be obtained by interrupting the synthesis schematically drawn in Fig. 12-6 at any desired generation. Instead of coupling Behera's amine to the carboxylic end groups, building block **A** should be coupled. Acid-catalyzed hydrolysis of the terminal *t*-BOC moieties yields dendrimers with amine terminal functions. In a similar fashion, building block **B** can be used to acquire 'arborols' of various generations. After building block **B** has been introduced by applying the standard amidation conditions, the acetyl masking groups can be removed by a simple base-catalyzed hydrolysis ( $K_2CO_3$ , EtOH) to afford the corresponding dendritic polyols.

The three series of cascade polyamides possessing either acidic ( $-COOH$ ), neutral ( $-OH$ ), or basic ( $-NH_2$ ) termini have been

studied by diffusion-ordered 2D NMR (DOSY) (Young et al., 1994). In this NMR technique, a pulsed field gradient is employed to allow the measurement of diffusion coefficients (Morris and Johnson, 1993). The diffusion coefficient of a polymer in a solvent ( $D$ ) is related to the effective hydrodynamic radius ( $R_H$ ) of this polymer by the Stokes–Einstein equation, i.e.,  $R_H = k_B T / (6D\pi\eta)$ , in which  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $\eta$  is the viscosity of  $D_2O$  at temperature  $T$ . The hydrodynamic radii of the three types of dendrimers have been determined at different pH values, showing that the acidic and basic dendrimers swell or shrink upon pH change, whereas the neutral dendrimers do not adjust their size in response to a pH stimulus. Apparently, charge repulsion at the surface forces the dendrimers to more extended conformations, whereas the absence of such repulsion facilitates backfolding of the flexible branches.

The various masked dendritic materials have been purified by aqueous extraction and column chromatography, whereas the dendrimers with the carboxylic acid, amine, or alcohol termini have been worked up by dialysis procedures and, in some cases, preparative reversed phase HPLC techniques. All dendrimers have been characterized by NMR methods, IR, elemental analysis, and SEC, showing that the obtained

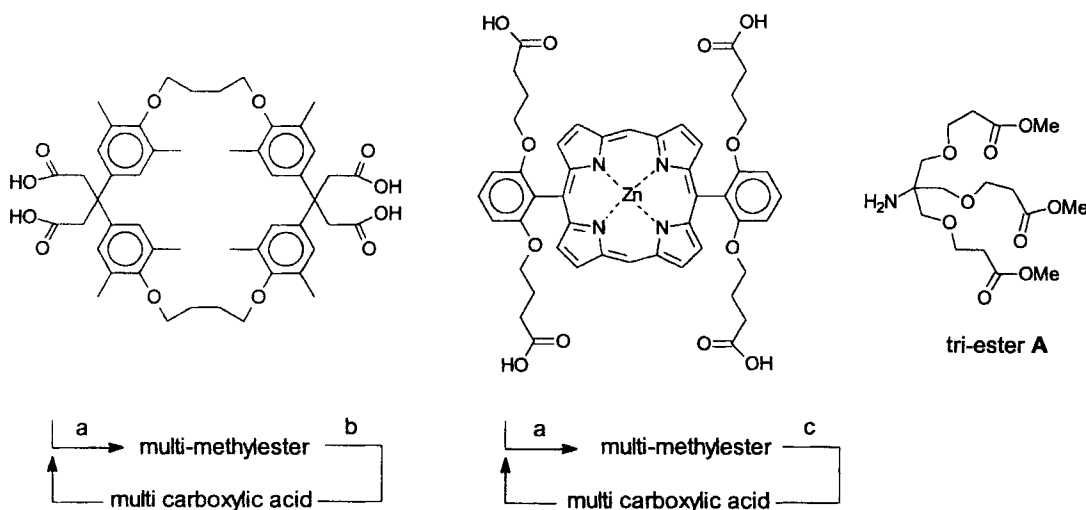


**Figure 12-8.** Newkome's syntheses of dendrimers with amine (left route) or alcohol (right route) end functionalities. In this example, the starting compound is a tetrafunctional acid; multi-acid functionalized dendrimers obtained from the iterative synthesis shown in Fig. 12-6 can also be used as starting compounds.

data are in agreement with the assigned structures. However, the used characterization techniques are not suited to determine the presence of small amounts of defect structures, especially when higher generation material is considered. In fact, defect structures should be expected in the higher generations, since standard amidation conditions are used in the iterative syntheses of these materials. Such amidation conditions are routinely applied in Merrifield syntheses of polypeptides, and the phenomenon of

the expression of small defects is well known in this area. For example, the 124 amino acid ribonuclease has been synthesized to 17% purity after 369 chemical conversions (the other 83% of the material possess one or more defect in the amino acid sequence) (Solomons, 1996).

Newkome has reported titration experiments indicating that a high level of purity is routinely obtained with the applied synthetic procedure (Newkome et al., 1997). Detailed mass spectrometry data on the de-

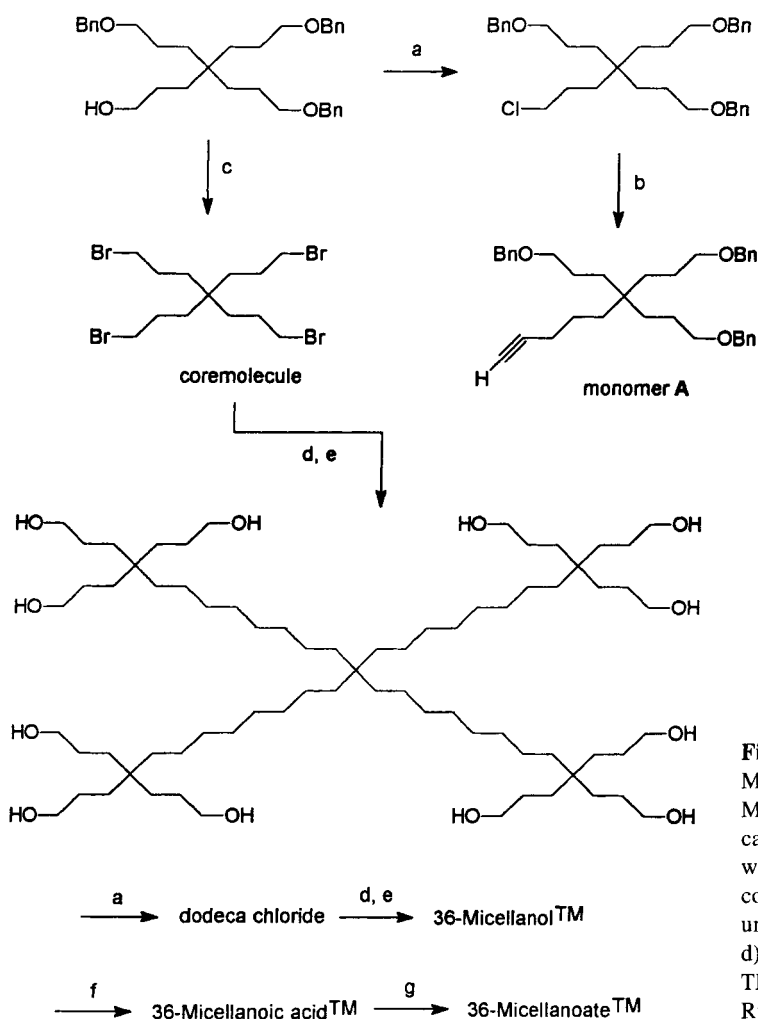


**Figure 12-9.** Dendrimers with a cyclophane or a porphyrin core, as synthesized by Diederich. The 'dendrophanes', i.e., cyclophanes covalently linked to a dendritic substructure, are receptor molecules (Mattei et al., 1995). The porphyrin derivatives can be regarded as the synthetic analogs of globular heme proteins (Dandliker et al., 1994). a) A, DCC, 1-HBT, THF; b) LiOH, THF/MeOH/H<sub>2</sub>O; c) LiOH, MeOH/H<sub>2</sub>O.

scribed dendritic structures have not been reported by Newkome. Diederich, however, has produced similar dendritic systems that have been analyzed by fast atom bombardment (FAB) and matrix-assisted laser desorption time-of-flight (MALDI-TOF) mass spectroscopy (Mattei et al., 1995; Dandliker et al., 1994). A tri-methyl ester building block and a four-directional porphyrin or cyclophane core have been employed to construct the targeted molecules (see Fig. 12-9). Analogous to the iterative dendrimer syntheses described by Newkome, standard amidation conditions (DCC, 1-HBT, DMF) have been used by Diederich. Purification by preparative gel permeation chromatography (GPC) has afforded dendrimers up to generation G<sub>3</sub>. The MALDI-TOF mass spectrum of the G<sub>2</sub> material possessing the porphyrin core indicates a base peak corresponding to the molecular ion, and small additional peaks corresponding to defect ions missing one or more branch units are observed. Consequently, these mass data

testify that the synthesis of small amounts of defect dendritic structures cannot be circumvented when the divergent approach, as introduced by Newkome, is followed. In a broader sense, these data indicate that all dendrimers prepared via divergent methods will, to a certain extent, suffer from these defect structures.

Apart from the structures shown in Figs. 12-4 to 12-6 and Fig. 12-8, Newkome (Newkome et al., 1991b) has reported numerous other dendritic systems such as, for example, Micellanol and Micellanoic acid (see Fig. 12-10). These all-saturated structures with hydrophobic hydrocarbon interiors and hydrophilic alcohol or carboxylic acid exteriors have been prepared by using the tri-benzylic alcohol depicted in Fig. 12-10. This molecule is prepared in seven steps from nitromethane and serves as a precursor to both the tetrabromide core and the three-directional acetylene branching unit. Micellanoic acid can be modified with tetramethylammonium hydroxide to yield Mi-



**Figure 12-10.** The synthesis of Micellanol, Micellanoic acid, and Micellanoate. Micellanoate has 36 carboxylate end functionalities with 36 tetramethylammonium counter cations. a)  $\text{SOCl}_2$ ; b) lithium acetylide; c)  $\text{HBr}$ ,  $\text{H}_2\text{SO}_4$ ; d) monomer A, HMPA, LDA, TMEDA; e)  $\text{Pd/C}$ ,  $\text{H}_2$ ,  $\text{EtOH}$ ; f)  $\text{RuO}_4$ ; g)  $\text{N}(\text{CH}_3)_4\text{OH}$ .

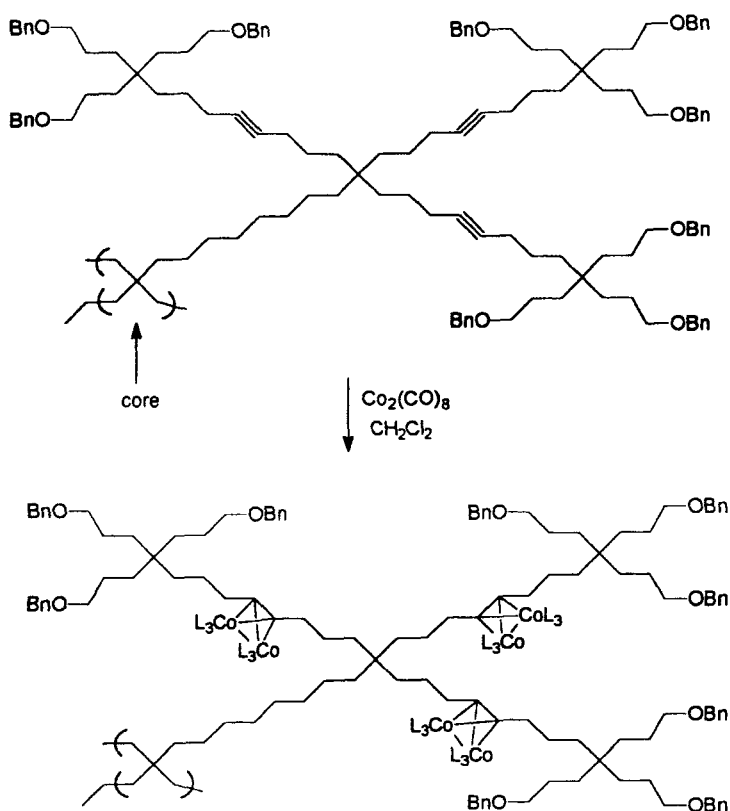
cellanoate. This unimolecular micelle is able to carry hydrophobic guest molecules (Newkome et al., 1991 c).

The versatility of the synthetic route to the various micellar structures is demonstrated by the modification of their polyalkyne precursors. Reaction of the alkyne moieties with decaborane ( $\text{B}_{10}\text{H}_{14}$ ) (Newkome et al., 1994 a) or dicobalt octacarbonyl ( $\text{Co}_2\text{CO}_8$ ) (Newkome and Moorefield, 1994 b) affords dendrimers with site-specified functionalities within their structure (see Fig. 12-11).

### 12.2.1.2 Tomalia's Starburst Dendrimers

Tomalia and co-workers (Tomalia et al., 1985, 1986) have introduced the so-called PAMAM (polyamidoamine) 'Starburst dendrimers'. These dendrimers are built in a repetition of two synthetic steps: a Michael addition of methyl acrylate on an amine followed by an amidation with ethylenediamine on the resulting methyl ester. This branching theme has been utilized starting with various core molecules such as (most



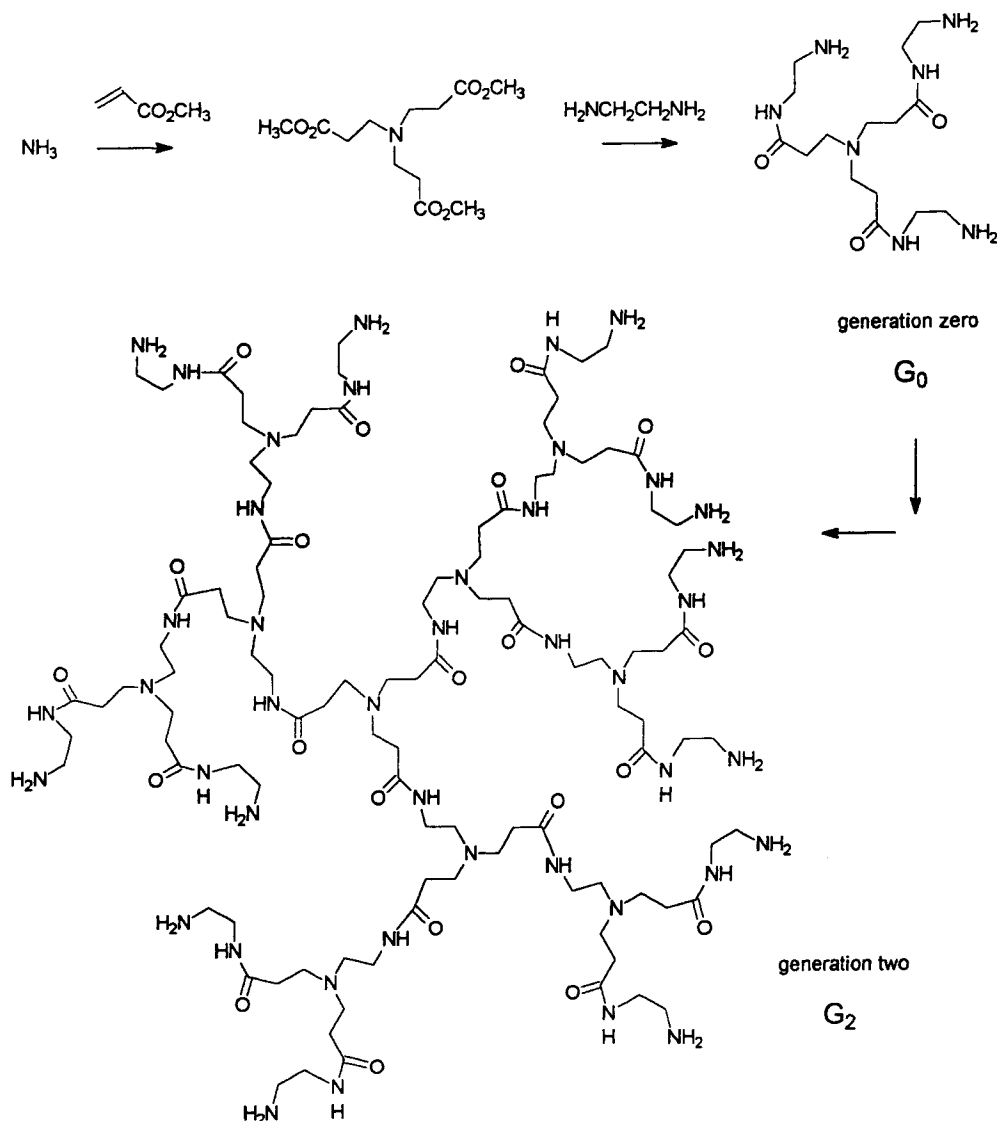


**Figure 12-11.** The conversion of an alkyne-bearing precursor of Micellanol to a cobalt-functionalized dendrimer. In a similar fashion, borane derivatives can be made [using  $\text{B}_{10}\text{H}_{14}$ , MeCN in toluene instead of  $\text{Co}_2(\text{CO})_8$  in  $\text{CH}_2\text{Cl}_2$ ]. L = CO-ligand.

importantly)  $\text{NH}_3$  and ethylenediamine. Aryl triesters (Tomalia and Dewald, 1985, a hexa-ester (Evans et al., 1993), and a wide variety of difunctional molecules (Tomalia et al., 1993) have also been used as cores. The applied synthesis allows modification of the dendrimer exterior (Tomalia et al., 1993; Meltzer et al., 1992), for instance, hydroxyl-terminated dendrimers have been produced by using 2-aminoethanol as the amidation reagent (Meltzer et al., 1992). The first published PAMAM dendrimer initiates from an  $\text{NH}_3$  core molecule (see Fig. 12-12) (Tomalia et al., 1986). The addition of methyl acrylate to a methanolic  $\text{NH}_3$  solution affords the tri-ester in a 98% yield. Subsequent amidation in methanol using an excess of ethylenediamine gives the so-called zero generation PAMAM den-

dimer in a 99% yield<sup>1</sup>. Repeating this sequence of reactions, dendrimers up to generation  $\text{G}_{4.5}$  have been synthesized, with yields of intermediate generations always exceeding 91%. In articles of later date, dendrimers of even higher generations (up to  $\text{G}_9$ ) have been reported (Meltzer et al., 1992). Work-up procedures involve the in vacuo removal of volatiles and, for the higher generation materials, dialysis and ultracentrifugation. The PAMAM dendrimers are isolated as viscous syrups or glasses.

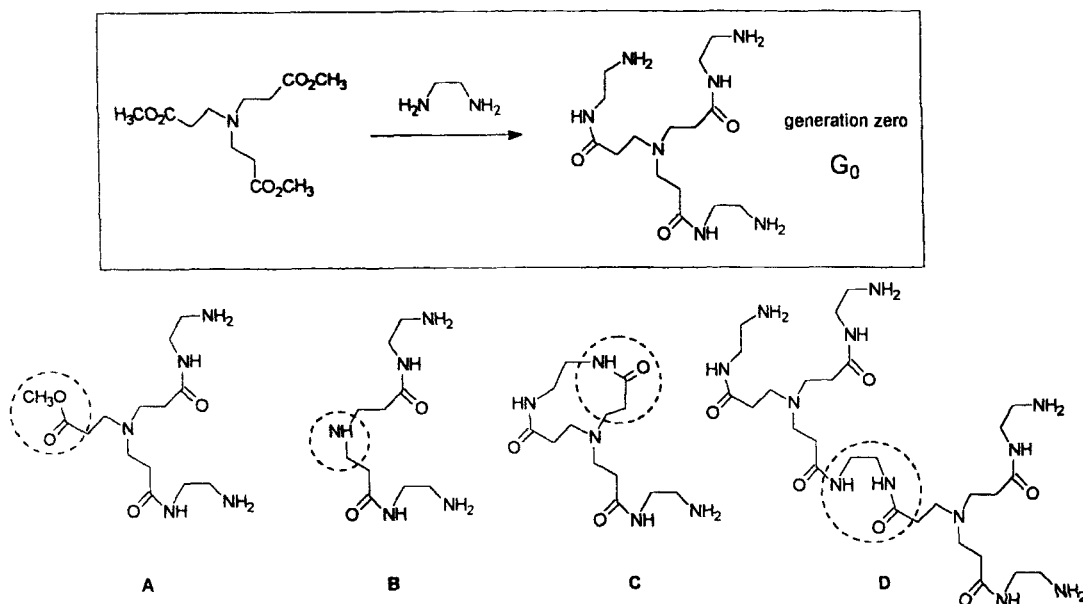
<sup>1</sup> In the initial article (Tomalia et al., 1986), this tri-amine is called the first generation PAMAM dendrimer. Later (Tomalia et al., 1990), this convention was changed, effectively reducing the numbering of every generation by one. Here, the latest numbering convention is used. In any case, amines are "whole" generations and esters are "half" generations.



**Figure 12-12.** The synthesis of PAMAM dendrimers comprises a sequence of (i) Michael additions with methyl acrylate and (ii) amidations with ethylene diamine.

Optimization of both steps in the synthesis of the PAMAM dendrimers is of key importance to the purity of the final product. Therefore these two steps have been examined, focusing on possible side reactions (Smith et al., 1987). First, the applied Michael addition has been found to be fast, proceeding without the formation of significant amounts of by-products. Therefore this re-

action is typically executed at 20 °C, applying only a small molar excess of methyl acrylate (molar excesses of typically 10% have been used). Second, the amidation reaction has been found to be a slower process, implying that total conversion is problematic. Moreover, unwanted side reactions such as retro-Michael reactions, intramolecular lactam formations, and intermolecular



**Figure 12-13.** Top: the correct amidation to PAMAM dendrimer G<sub>0</sub>. Unwanted reaction products arise from: incomplete amidations (A), retro-Michael reactions (B), intramolecular lactam formations (C), and intermolecular amidations (D).

coupling reactions compete in this amidation step (see Fig. 12-13). In order to estimate the importance of these side reactions, a combined experimental and theoretical study using <sup>13</sup>C NMR spectroscopy, size exclusion chromatography (SEC), mass spectrometry, and statistical modeling has been carried out (Smith et al., 1987). It was found that the retro-Michael reaction could be largely suppressed by applying low reaction temperatures and providing a sufficiently methanolic reaction medium. Intermolecular linking reactions could be overpowered by using a large excess of ethylenediamine. However, at higher generations, the required excess of ethylenediamine to prohibit linking reactions was calculated to be experimentally unfeasible. The formation of intramolecular lactam adducts, which were observed by mass spectrometry and <sup>13</sup>C NMR, has not been studied in detail. Presumably, lactam formation can be minimized by using ethylenediamine in excess in a metha-

nolic reaction medium. Thus, the study has resulted in amidation conditions that involve the use of large excesses of ethylenediamine ('exhaustive amidation'). Furthermore, long reaction times (typically days), a methanolic medium, and low temperatures (0–5 °C) are required in this step.

The ideal growth of dendrimers is stopped at the so-called dense-packed state, as pointed out in a theoretical exposition by de Gennes (de Gennes and Hervet, 1983). The dense-packed state is reached when the surface area per end functionality equals the van der Waals dimensions of such an end functionality. The generation  $m_1$  at which full congestion is reached can be derived from a simple equation ( $P$  = branch segment length) (de Gennes and Hervet, 1983).

$$m_1 = 2.88 \times (\ln P + 1.5). \quad (12-1)$$

Thus, for PAMAM dendrimers, the dense-packed generation ( $m_1$ ) has been predicted to lie in-between generations G<sub>9</sub> and G<sub>10</sub>.

The characterization of PAMAM dendrimers has been carried out applying various techniques including  $^1\text{H}$  NMR,  $^2\text{H}$  NMR, and  $^{13}\text{C}$  NMR spectroscopy (Meltzer et al., 1992; Smith et al., 1987), SEC (Smith et al., 1987), intrinsic viscosity measurements (Tomalia et al., 1990), and electrospray ionization mass spectrometry (Kallos et al., 1991) (ESI-MS). The intrinsic viscosity ( $\eta$ ) measurements on the PAMAM materials have been proposed to support the idea of an increasingly packed dendrimer surface. Initially, the intrinsic viscosity increases as a function of the molar mass, but at generation  $G_4$ , the onset of a viscosity decline is observed. It is argued that from generation  $G_4$  on, surface congestion starts to reduce the optimum surface-solvent interactions, and therefore the dendrimer is beginning to act more like an Einstein spheroid. Another explanation for the decreasing intrinsic viscosity as a function of the molecular weight is simpler. With increasing molecular weight, the density of dendrimers increases, thus it is plausible that the intrinsic viscosity decreases accordingly ( $[\eta] = (\eta_{\text{spec}}/c)_{c \rightarrow 0}$ ;  $c$  in mass per volume) (Fréchet et al., 1996).

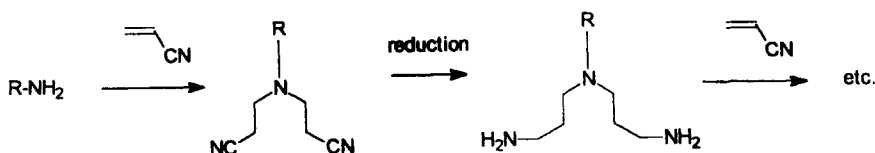
Electrospray ionization mass spectrometry (ESI-MS) is extremely useful in the determination of the exact nature of the produced PAMAM materials, especially with respect to the higher generations. Although higher generation dendrimers have been analyzed with ESI-MS, detailed and minutely examined ESI-MS data are only reported on the PAMAM dendrimers of generations as high as generation  $G_4$  (this is the material with, ideally, 48 amine end groups, corresponding to a molecular weight of 10632 Dalton). The analysis of  $G_4$  has shown the presence of imperfect components, resulting from incomplete reaction and lactam formation reactions. Nevertheless, a polydispersity of 1.0007 has been calculated for

$G_4$ . As opposed to the characterization of dendrimers in terms of polydispersity, it is also possible to directly calculate the dendritic purity of the perfect dendrimer from the ESI-MS data available (the dendritic purity is defined as the percentage of error-free dendrimer molecules). Performing such a calculation, a purity of ca. 8% can be derived for from the  $G_4$  dendrimer.

The PAMAM dendrimers were the first dendrimers available for detailed studies. Therefore other research groups have also reported on the characteristics of PAMAM dendrimers. Furthermore, these dendrimers have been used to probe many of the properties that have been proposed for dendritic structures. For those interested in the mentioned studies, we would like to refer to the original publications (Caminati et al., 1990, 1991; Ottaviani et al., 1995; Miller et al., 1995; Farin et al., 1990; Watanabe and Regen, 1994), and to several excellent reviews (Newkome et al., 1996; Issberner et al., 1994; Tomalia et al., 1990; Ardoin and Astruc, 1995; Fréchet et al., 1996; Malmström and Hult, 1997).

### 12.2.1.3 Poly(propylene imine) Dendrimers

Acrylonitrile is a convenient building block in the synthesis of dendrimers, as was recognized for the first time by Vögtle in 1978 (see Fig. 12-14) (Buhleier et al., 1978). Unfortunately, his attempts at producing so-called 'cascade' molecules on the basis of this building block were severely hampered by difficulties in the reduction of the nitrile moiety and by complications in the subsequent purification of the amines. Independently, these problems have been solved by Mülhaupt (Wörner and Mülhaupt, 1993) and de Brabander (de Brabander-van den Berg and Meijer, 1993), who showed



**Figure 12-14.** The reaction sequence, as introduced by Vögtle, used for the production of poly(propylene imine) dendrimers.

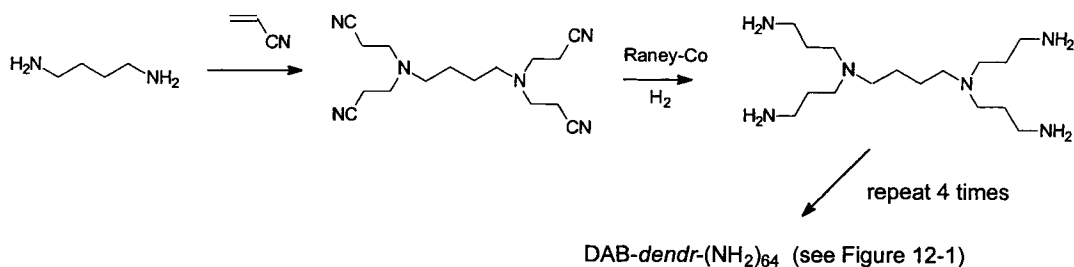
that the application of heterogeneous hydrogenation catalysts (i.e., Raney-nickel and Raney-cobalt catalysts, respectively) can overcome the previously mentioned problems. Apart from the use of different hydrogenation catalysts, the syntheses of Mülhaupt and de Brabander make use of two different core molecules [ $NH_3$  and 1,4-diaminobutane (DAB), respectively], resulting in poly(propylene imine) dendrimers with different numbers of end functionalities. Both Mülhaupt and de Brabander have applied comparable reaction conditions for the two consecutive synthetic steps, but the approach of de Brabander has been optimized, facilitating the production of the poly(propylene imine) DAB dendrimers on a large scale. Apart from generation  $G_{0.5}$ <sup>2</sup>, which is a crystalline solid, all other generations of poly(propylene imine) DAB dendrimers are colorless oils. The DAB-*dendr*-(CN)<sub>x</sub> generations are soluble in organic solvents, whereas the DAB-*dendr*-(NH<sub>2</sub>)<sub>x</sub> generations dissolve in H<sub>2</sub>O and MeOH. All poly(propylene imine) dendrimers up to  $G_5$  (64 amine end groups) are now commercially available.

Production of poly(propylene imine) DAB dendrimers, comprises (i) the double

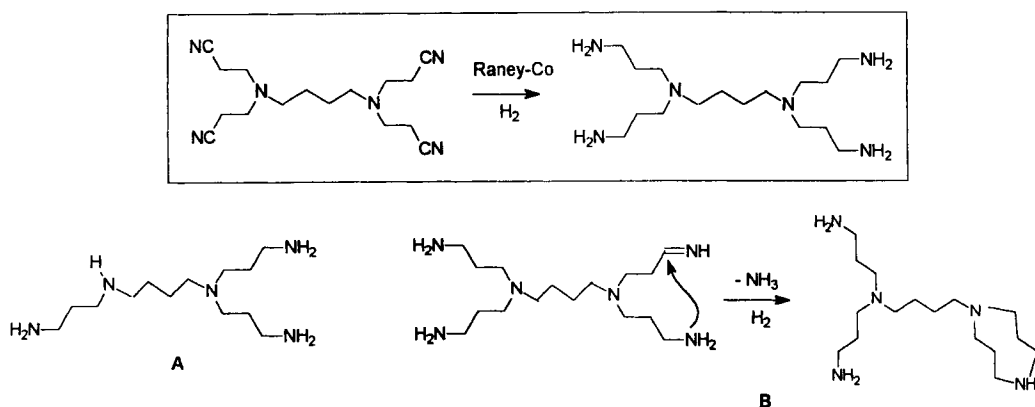
Michael addition of acrylonitrile on an amine (cyanoethylation) and (ii) hydrogenation of the resulting nitrile (see Fig. 12-15). The cyanoethylation is executed with 2.5–4 equivalents of acrylonitrile per primary amine and is performed in H<sub>2</sub>O. The first equivalent is added and reacts at room temperature, whereas the reaction of the second requires 80 °C. Even for the higher generation amines, this reaction is quite smooth and complete conversion is achieved within a few hours (incomplete cyanoethylation can readily be concluded from surplus <sup>13</sup>C NMR signals).

Hydrogenation of the various DAB-*dendr*-(CN)<sub>x</sub> materials is performed in H<sub>2</sub>O, applying H<sub>2</sub> pressures of 30–70 bar and using the Raney-cobalt catalyst. Hydrogenation is the difficult step in the production of poly(propylene imine) dendrimers, mainly because unwanted side reactions can occur. These side reactions are (i) the retro-Michael reaction and (ii) the intramolecular addition of amines to imines – these are intermediates in the hydrogenation process – resulting in the formation of cyclic species and NH<sub>3</sub> (see Fig. 12-16). The products of the retro-Michael reaction can be observed in the <sup>13</sup>C NMR spectrum, in which an extra set of signals becomes visible. Slight adjustments of the hydrogenation conditions at every generation can minimize the occurrence of the retro-Michael reaction. The formation of cyclic species can be minimized by applying ammonia in the reaction mixture. It should be stressed, however, that the process window for an ideal

<sup>2</sup> The numbering and notation convention for the poly(propylene imine) DAB dendrimers is as follows: The nitrile-terminated components are “half” generations, whereas the amine-terminated components are “whole” generations. The compound with four nitrile functions is generation  $G_{0.5}$  and is denoted as DAB-*dendr*-(CN)<sub>4</sub>; the following generations are DAB-*dendr*-(NH<sub>2</sub>)<sub>4</sub>, DAB-*dendr*-(CN)<sub>8</sub>, DAB-*dendr*-(NH<sub>2</sub>)<sub>8</sub>, etc.



**Figure 12-15.** The divergent synthesis of poly(propylene imine) DAB dendrimers starting from diaminobutane (DAB). The sequence comprises (i) a cyanoethylation and (ii) a Raney-cobalt reduction.



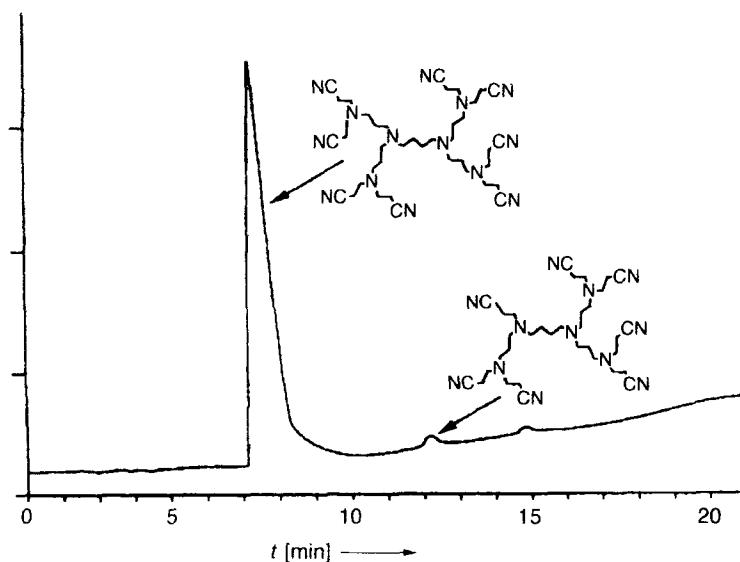
**Figure 12-16.** Top: the correct hydrogenation to DAB-*dendr*-(NH<sub>2</sub>)<sub>4</sub>. Unwanted reaction products arise from (A) retro-Michael reactions and, (B) intramolecular amine formations. Products from incomplete hydrogenation might also be formed.

hydrogenation is small, since the mentioned side reactions can occur easily.

Since both reactions in the production sequence of poly(propylene imine) dendrimers are performed in H<sub>2</sub>O, it is not required that all the individual intermediates be isolated. After hydrogenation, the solution is filtered, the concentration of the filtrate is adjusted by water evaporation, and the Michael addition is started. After the Michael addition, azeotropic distillation of excess acrylonitrile (with H<sub>2</sub>O) is carried out, followed by washing the product with H<sub>2</sub>O. Finally, the concentration of the nitrile-terminated product is adjusted to perform the next hydrogenation. Recently, solvents used in

both reaction steps have been modified, improving the purity of the products without decreasing the attractiveness of the synthesis (DSM Research, 1997).

The poly(propylene imine) DAB dendrimers have been characterized by a range of techniques (de Brabander-van den Berg and Meijer, 1993), including various NMR spectroscopy methods [<sup>1</sup>H NMR, <sup>13</sup>C NMR, and <sup>15</sup>N NMR (Van Genderen et al. 1994)], IR spectroscopy, high pressure liquid chromatography (HPLC), SEC, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and intrinsic viscosity measurements. HPLC data on DAB-*dendr*-(CN)<sub>8</sub> have shown the presence of a



**Figure 12-17.** HPLC chromatogram of DAB-dendr-(CN)<sub>8</sub>.

small amount of DAB-dendr-(CN)<sub>7</sub>, on the basis of which an average selectivity per conversion of 99.8% could be derived for the first three steps (see Fig. 12-17).

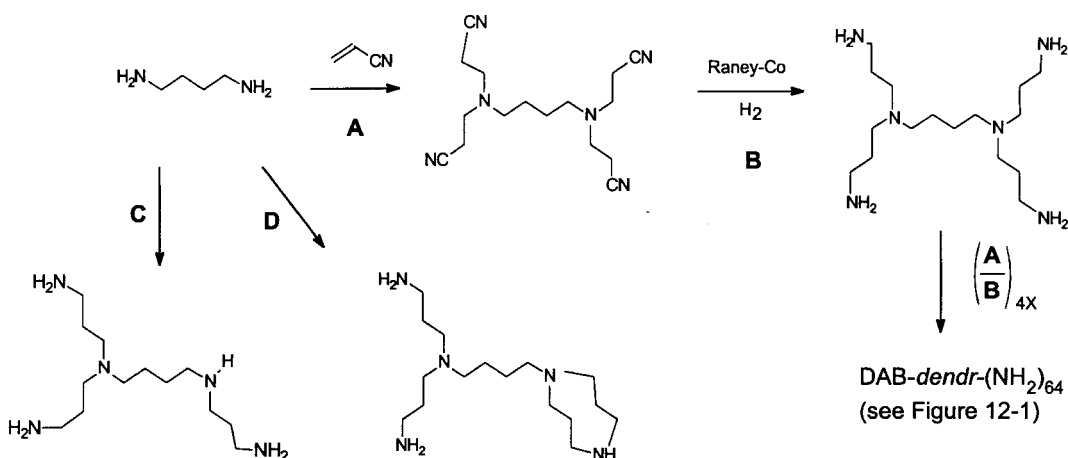
DSC results have shown that the glass transition temperature ( $T_g$ ) of the poly(propylene imine) DAB dendrimers is low and increases with increasing generation. The nitrile-terminated half generations have higher  $T_g$  values, as expected on the basis of the dipole-dipole interactions of the CN moieties<sup>3</sup>. Further thermal analysis shows that the amine-terminated materials are remarkably stable. TGA data show increasing stability for every next generation, e.g., TGA<sub>max</sub> values of 330 °C and 470 °C have been determined for G<sub>1</sub> and G<sub>4</sub>, respectively. The nitrile-terminated materials are less stable due to thermally induced retro-Michael reactions. The intrinsic viscosity ( $\eta$ ) of the nitrile-terminated components shows an initial increase upon a molecular weight

increase. However, on going from G<sub>3.5</sub> to G<sub>4.5</sub> and G<sub>5.5</sub>, a viscosity drop is measured. Such a development in the intrinsic viscosity as a function of molecular weight is typical for dendritic materials (Tomalia et al., 1990; Mouray et al., 1992). The spectral data (primarily NMR data) of the isolated poly(propylene imine) DAB dendrimers are consistent with the proposed dendrimer structures. However, especially at higher generations, the applied spectroscopic tools are no longer suitable for the detection of small amounts of defect structures. Therefore a detailed electrospray ionization mass spectrometry (ESI-MS) study has been performed to elucidate the exact nature of the commercially available poly(propylene imine) DAB dendrimers (Hummelen et al., 1997). In the following, the results of this study will be described and discussed.

#### *Electrospray Ionization Mass Spectrometry (ESI-MS) Analysis of Poly(propylene imine) Dendrimers*

The poly(propylene imine) dendrimers with either the amine or the nitrile end group

<sup>3</sup> The DAB-dendr-(NH<sub>2</sub>)<sub>i</sub> materials of generation G<sub>2</sub> and higher have  $T_g$  values of ca. -65 °C; the DAB-dendr-(CN)<sub>i</sub> materials of generation G<sub>1.5</sub> and higher have  $T_g$  values of ca. -50 °C.



**Figure 12-18.** The synthesis of poly(propylene imine) dendrimers (reactions **A** and **B**) and alternative pathways **C** and **D**. Path **C** illustrates a “missed” Michael addition (either by an incomplete cyanoethylation or by a retro-Michael reaction). Path **D** illustrates a cyclization reaction. Paths **C** and **D** describe defect reactions on going from one amine generation to the next.

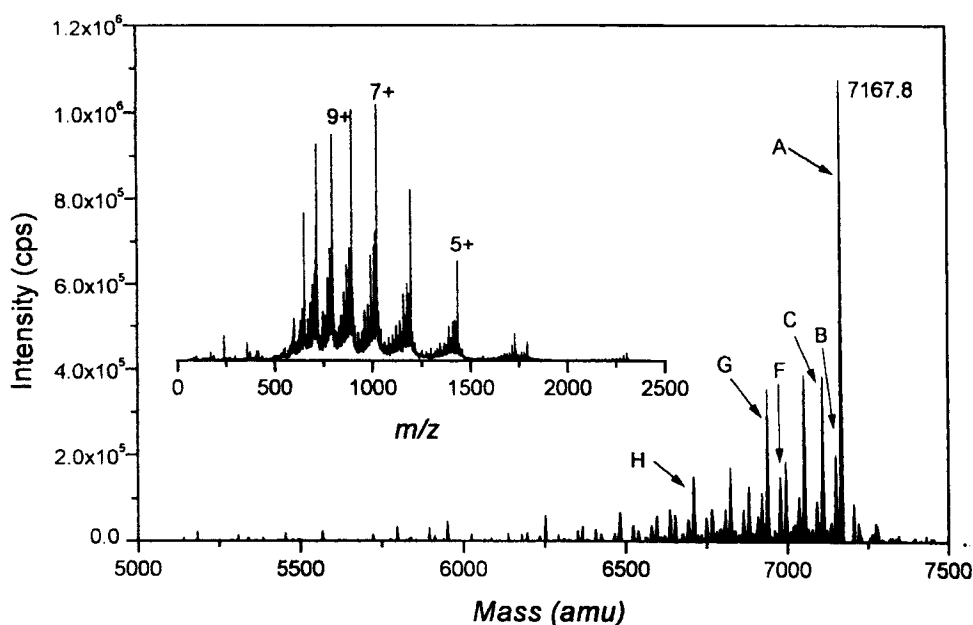
have been synthesized on a large scale following the reaction sequence given in Fig. 12-15. The alternating sequence of Michael additions and hydrogenation reactions leads in ten steps from diaminobutane (DAB) to  $\text{DAB-dendr}-(\text{NH}_2)_{64}$ . After 248 successful consecutive reactions, the ideal structure, as given in Fig. 12-1, is formed. However, the probability of (i) incomplete Michael additions and (ii) the formation of cyclic structures or retro-Michael reactions during hydrogenation must be acknowledged. These three side reactions can be incorporated in two side paths **C** and **D** (see Fig. 12-18)<sup>4</sup>. In conclusion, the dendritic product should suffer from a small number of statistical defects and, hence, should have a polydispersity, even in the case where the reactions involved are optimized to the extreme.

<sup>4</sup> Paths **C** and **D** are the overall results of side reactions occurring from one amine generation to the next. Note that path **D** is an actual side reaction in the hydrogenation procedure and that path **C** is a pathway which accounts for both an incomplete Michael addition and a retro-Michael reaction.

Both types of poly(propylene imine) dendrimer, i.e.,  $\text{DAB-dendr}-(\text{CN})_x$  and  $\text{DAB-dendr}-(\text{NH}_2)_x$ , are polar and poly-basic components which are partially protonated when dissolved in methanol–water mixtures. This property allows for the direct analysis of the dendrimer solutions by positive ion ESI-MS (Hummelen et al., 1997). The actual and deconvoluted ESI-MS spectra of  $\text{DAB-dendr}-(\text{NH}_2)_{64}$  are given in Fig. 12-19. The measured spectrum shows different clusters of peaks, every peak corresponding to a component with a certain  $m/z$  value and each cluster corresponding to dendrimers with a particular charge  $z$  ( $z = 4, 5, \dots, 11, 12$ ). No counterion interactions are observed. Deconvolution<sup>5</sup> using standard methods gives a spectrum in which the largest peak at  $M_R = 7168$  corresponds to the perfect fifth generation dendrimer  $\text{DAB-}$

<sup>5</sup> Deconvolution, which is a standard procedure in ESI-MS, converts the measured  $m/z$  values of the components to the  $m$  values of the components by collecting the clusters in so-called envelopes. Every envelope corresponds to a  $z$  value, so the  $m$  value can be calculated.



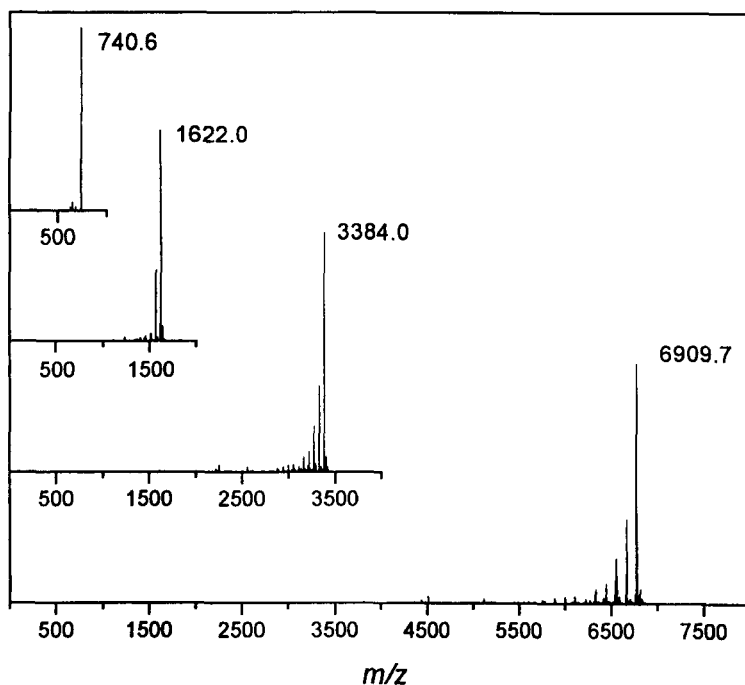


**Figure 12-19.** The experimental (inset) and deconvoluted ESI-MS data on DAB-*dendr*-(NH<sub>2</sub>)<sub>64</sub>. For the explanation of A, B, C, F, G, and H the reader is referred to Fig. 12-23 and to Table 12-1.

*dendr*-(NH<sub>2</sub>)<sub>64</sub>. Furthermore, a series of peaks is found, in which every peak is positioned at discrete mass intervals of  $\Delta M_R = n \times 57.1$  from the perfect dendrimer at  $M_R = 7168$ . These peaks correspond to dendrimers with  $n$  missing propylamine units (via path C; see Fig. 12-18). Additionally, the peak at  $M_R = 7151$  ( $\Delta M_R = 17$ ) is assigned to the dendritic component with 62 primary amine end groups and one cyclic secondary amine structure; this dendrimer is formed as a result of the splitting off of ammonia via path D (Fig. 12-18). Again, this peak is related to a series of peaks that can be found at mass intervals of  $\Delta M_R = n \times 57.1$  from  $M_R = 7151$ . In short, all peaks in the deconvoluted spectrum can be assigned to defect structures arising from (a combination of) the defect pathways outlined in Fig. 12-18.

In order to fully understand the origin of the smaller peaks, ESI-MS spectra of all

generations with both end functionalities have been recorded. The deconvoluted spectra of the DAB-*dendr*-(CN)<sub>*x*</sub> series with  $x = 8 - 64$  are given in Fig. 12-20. The lowest generations (up to  $x = 8$ ) are seemingly defect-free (e.g., a molecular ion peak is found at  $M_R = 740.6$  for  $x = 8$ ). For the nitrile-terminated, third generation DAB-*dendr*-(CN)<sub>16</sub>, the perfect dendrimer structure is found at  $M_R = 1622.0$ , while at least one defect structure is recorded at 1569.0 ( $\Delta M_R = 53$ ; missing acrylonitrile). For the fourth and fifth generation, a repetition of defects at intervals of  $\Delta M_R = 53$  is found, assigned to missing acrylonitrile units. Peaks at  $\Delta M_R = 17$  originate from cyclization reactions in the synthesis of the earlier generations (path D), whereas the peaks at  $\Delta M_R = 57$  originate from “missed” acrylonitrile units in earlier generations (path C). The recorded peaks are not the result of fragmentation in the apparatus, as an MS/MS



**Figure 12-20.** The deconvoluted ESI-MS data of DAB-dendr-(CN)<sub>x</sub> with, from left to right,  $x = 8, 16, 32,$  and  $64$ .

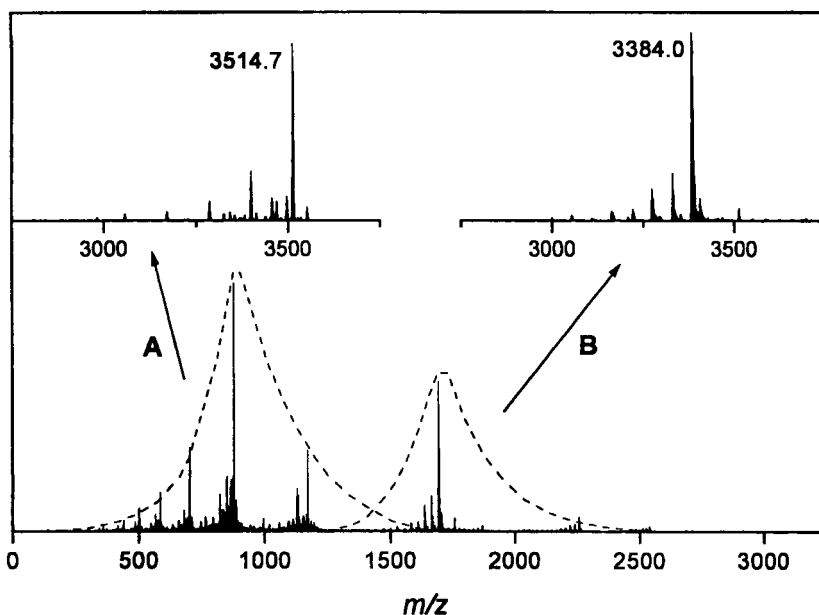
study on a number of dendrimers with small defects has shown <sup>6</sup>.

The spectra of the DAB-dendr-(NH<sub>2</sub>)<sub>x</sub> series have also been investigated in detail. Despite the fact that IR spectral data on the DAB-dendr-(NH<sub>2</sub>)<sub>x</sub> dendrimers sometimes indicate the presence of small amounts of residual CN groups, the deconvoluted ESI-MS spectra clearly show that shoulders at  $\Delta M_R = 4$  are not present. Remarkably, however, ESI-MS is indicative for the presence of traces of starting material DAB-dendr-(CN)<sub>x</sub> (for example, see the small cluster around  $m/z = 1728.7$  in Fig. 12-19). This observation was investigated with material ob-

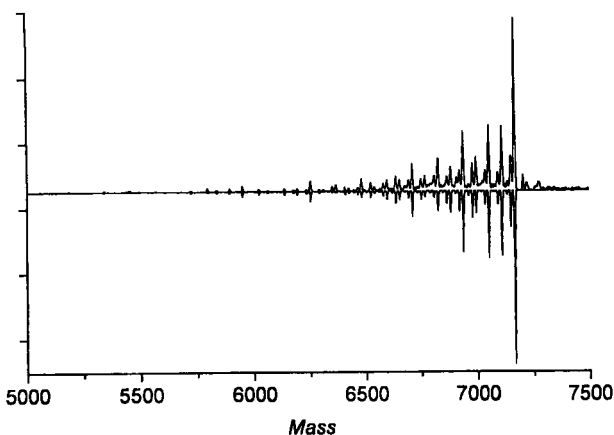
tained by the interruption of the hydrogenation of DAB-dendr-(CN)<sub>32</sub>. The ESI-MS spectra, using two envelopes to deconvolute the spectrum <sup>5</sup>, clearly show the presence of only two products: fully converted dendrimer and completely unreacted starting material (Fig. 12-21). Apparently, the nitrile dendrimer is fully hydrogenated before it is released from the surface of the Raney-Cobalt catalyst.

All defect structures found in the ESI-MS spectra of both series of poly(propylene imine) dendrimers originate from two side pathways (paths **C** and **D** in Fig. 12-18). Once the probability of both side paths is known from the individual ESI-MS spectra, it is possible to simulate the ESI-MS spectra for all generations, provided that the isotope distributions are accounted for, and assuming that the response factors are equivalent for the perfect and imperfect dendrimers. The simulated spectra can then be fitted on the actual deconvoluted spectra in an iterative process. The result of the DAB-

<sup>6</sup> Collision-activated dissociation (CAD) can be used to execute well-defined fragmentation processes. After filtering an ion in the first quadrupole of the instrument, this ion is fragmented by collision with neutral molecules in the gas phase. Finally, full characterization is performed with the second quadrupole. The fragmentation of defect DAB dendrimer structures has been studied and the results of this study will be published in due course.



**Figure 12-21.** ESI-MS spectrum of the interrupted hydrogenation of DAB-*dendr*-(CN)<sub>32</sub>. Inset **A** depicts the selective deconvoluted spectrum of the low mass region (see the deconvolution envelope). The totally converted material is clearly visible [DAB-*dendr*-(NH<sub>2</sub>)<sub>32</sub>,  $M_R$  = 3514.7]. Inset **B** depicts the selective deconvoluted spectrum of the high mass region. From this inset, unreacted DAB-*dendr*-(CN)<sub>32</sub> ( $M_R$  = 3384.0) is apparent.



**Figure 12-22.** The deconvoluted (upper graph) and the simulated (lower graph) ESI-MS spectrum of DAB-*dendr*-(NH<sub>2</sub>)<sub>64</sub>.

*dendr*-(NH<sub>2</sub>)<sub>64</sub> simulation is given in Figure 12-22, and an almost perfect fit is found with the actual spectrum, as given in Fig. 12-19. With this simulation in hand, all of the peaks in the spectrum can be assigned, e.g., a number of assignments are given in

Table 12-1. Additionally, the yield of both side paths in the formation of every amine generation can be determined (see Table 12-2). Thus the origin of the defect structures can be traced, and therefore the simulation results give an insight into the history of the

**Table 12-1.** Interpretation of the most prominent structures present in the mass spectrum of DAB-*dendr*-(NH<sub>2</sub>)<sub>64</sub>.

Isotope cluster at $M_R^a$	Structure <sup>b</sup>	Defect history <sup>c</sup>	Abundance <sup>d</sup> (%)
A = 7167.8	DAB- <i>dendr</i> -(NH <sub>2</sub> ) <sub>64(5)</sub>	no defects	100
B = 7150.6	DAB- <i>dendr</i> -(NH <sub>2</sub> ) <sub>62(5)</sub> (NH) <sub>1(5)</sub>	1* D at gen. 5	18.7
C = 7111.7	DAB- <i>dendr</i> -(NH <sub>2</sub> ) <sub>63(5)</sub> (NH) <sub>1(4)</sub>	1* C at gen. 5	36.2
D = 7053.2	DAB- <i>dendr</i> -(NH <sub>2</sub> ) <sub>62(5)</sub> (NH <sub>2</sub> ) <sub>1(4)</sub>	1* C at gen. 4	
	DAB- <i>dendr</i> -(NH <sub>2</sub> ) <sub>62(5)</sub> (NH) <sub>2(4)</sub>	2* C at gen. 5	35.8
E = 6995.6	DAB- <i>dendr</i> -(NH <sub>2</sub> ) <sub>61(5)</sub> (NH <sub>2</sub> ) <sub>1(4)</sub> (NH) <sub>1(4)</sub>	1* C at gen. 4 + 1* C at gen. 5	
	DAB- <i>dendr</i> -(NH <sub>2</sub> ) <sub>61(5)</sub> (NH) <sub>3(4)</sub>	3* C at gen. 5	17.1
F = 6979.1	DAB- <i>dendr</i> -(NH <sub>2</sub> ) <sub>61(5)</sub> 1 ring N <sup>3-4</sup>	1* D at gen. 4	
	DAB- <i>dendr</i> -(NH <sub>2</sub> ) <sub>59(5)</sub> (NH <sub>2</sub> ) <sub>3(4)</sub> (NH) <sub>1(5)</sub>	3* C at gen. 5 + 1* D gen. 5	14.1
G = 6939.7	DAB- <i>dendr</i> -(NH <sub>2</sub> ) <sub>60(5)</sub> (NH <sub>2</sub> ) <sub>2(4)</sub>	1* C at gen. 3	
	DAB- <i>dendr</i> -(NH <sub>2</sub> ) <sub>60(5)</sub> (NH <sub>2</sub> ) <sub>2(3)</sub>	2* C at gen. 4	37.8
H = 6711.2	DAB- <i>dendr</i> -(NH <sub>2</sub> ) <sub>56(5)</sub> (NH <sub>2</sub> ) <sub>4(4)</sub>	1* C at gen. 2	12.4

<sup>a</sup> The isotope clusters used are taken from the spectrum shown in Fig. 12-19. See also Fig. 12-23, in which the defect structures A, B, C, F, G, and H have been drawn; <sup>b</sup> The notation used: (NH<sub>2</sub>)<sub>x(y)</sub> means xNH<sub>2</sub> end groups at generation y; <sup>c</sup> The notation used: “3\* C at gen. 5” means three randomly missing Michael additions in the 5<sup>th</sup> generation (path C in Fig. 12-18), “1\* D at gen. 4” means one ring formation in the 4<sup>th</sup> generation (path D in Fig. 12-18, followed by normal growth; <sup>d</sup> Normalized abundance from the deconvoluted mass spectrum.

‘cascade’ synthesis of the poly(propylene imine) DAB dendrimers. In Fig. 12-23, the main defect structures in DAB-*dendr*-(NH<sub>2</sub>)<sub>64</sub> are shown.

The experimental ESI-MS data and the simulation data<sup>7</sup> can be used to calculate the polydispersity, the dendritic purity, and the branching efficiency of DAB-*dendr*-(NH<sub>2</sub>)<sub>64</sub>. Polydispersities of 1.0018 and 1.0024 and purities of 15% and 23% have been calculated from the deconvoluted and the simulated spectra, respectively. The polydispersity  $M_w/M_n$  is calculated the same way as it is normally done for macromolecules, whereas the dendritic purity is defined as the number of error-free dendrimers divided by all the dendritic structures. The branching efficiency, as typically defined and used for hyperbranched polymers (vide infra), is calculated at  $\alpha=0.987$ .

<sup>7</sup> For the polydispersity calculations, the region from 4000 to 7250 amu in the simulated mass spectrum has been used.

**Table 12-2.** Data of the DAB-*dendr*-(NH<sub>2</sub>)<sub>x</sub> series calculated from the simulated spectrum of DAB-*dendr*-(NH<sub>2</sub>)<sub>64</sub>.

Product	Path C (% per end group)	Path D (% per end group)	Dendritic purity (% of total)
DAB- <i>dendr</i> -(NH <sub>2</sub> ) <sub>4</sub>	1.0	0.0	96
DAB- <i>dendr</i> -(NH <sub>2</sub> ) <sub>8</sub>	1.0	0.55	86.7
DAB- <i>dendr</i> -(NH <sub>2</sub> ) <sub>16</sub>	1.65	0.50	63.8
DAB- <i>dendr</i> -(NH <sub>2</sub> ) <sub>32</sub>	0.97	0.77	41.3
DAB- <i>dendr</i> -(NH <sub>2</sub> ) <sub>64</sub>	0.58	0.65	23.1

This ESI-MS analysis raises the question of whether the statistical defects in dendrimers made by the divergent route should be discussed in terms of polydispersity or in terms of dendritic purity. Since it is preferable to use a terminology that is most informative, we would like to propose that in the case of dendrimers, in which the fully converted and perfect product is the dominant

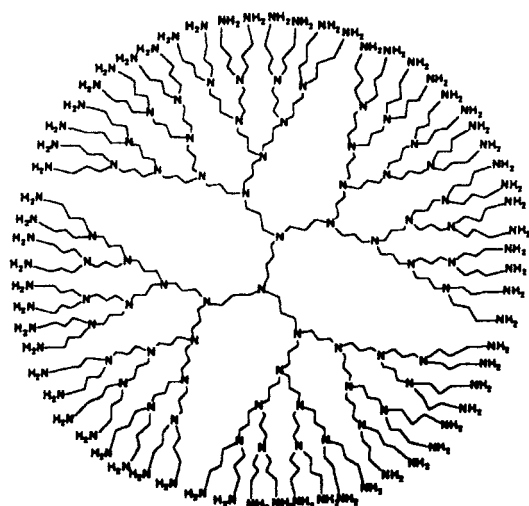
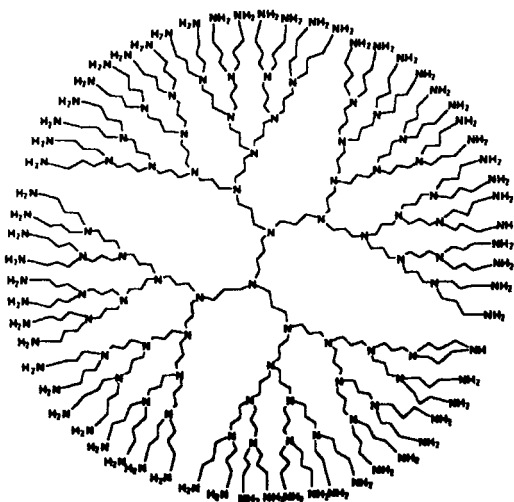
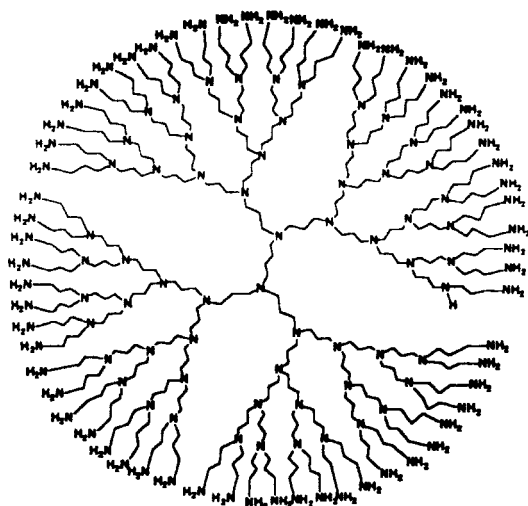
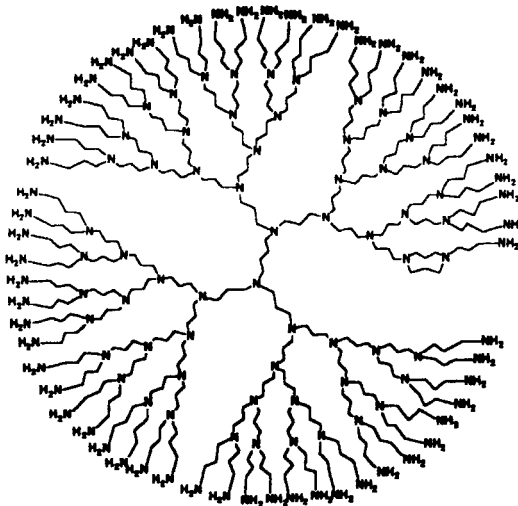
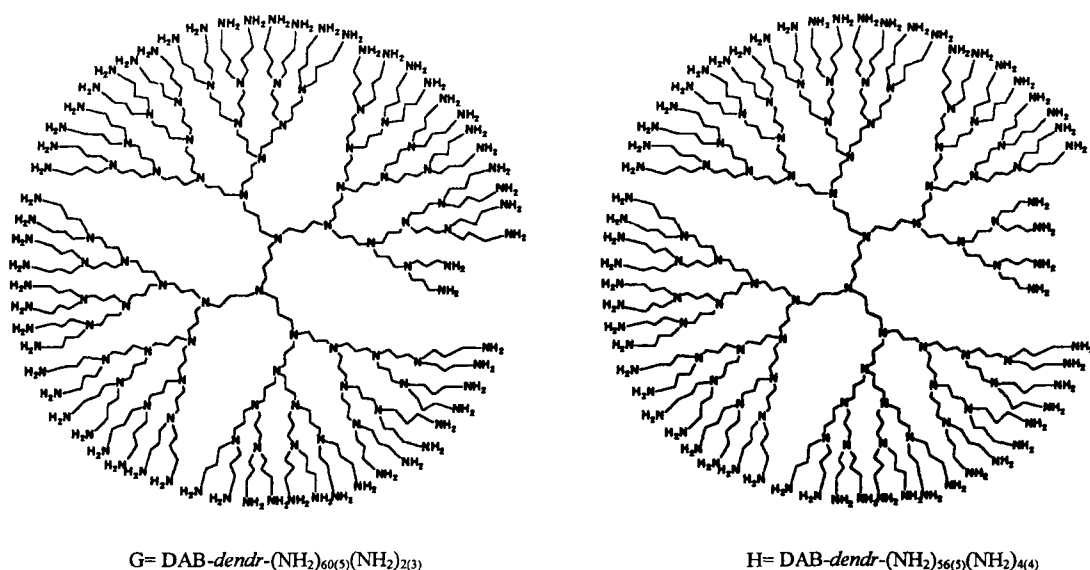
A=DAB-dendr-(NH<sub>2</sub>)<sub>64</sub>B=DAB-dendr-(NH<sub>2</sub>)<sub>62(5)</sub>(NH)<sub>1(5)</sub>C=DAB-dendr-(NH<sub>2</sub>)<sub>63(5)</sub>(NH)<sub>1(4)</sub>F=DAB-dendr-(NH<sub>2</sub>)<sub>61(5)</sub> 1 ring N<sup>3-4</sup>

Figure 12-23.

species, it is appropriate to present these products in terms of dendritic purity. The polydispersity of dendrimers is only useful when an imperfect dendrimer is the main product or when it is impossible to detect the individual molecules. In that case, it is

also difficult to use the methodology presented here, because too many defects in the different  $m/z$  regions will not allow an accurate deconvolution of the ESI-MS spectrum.



**Figure 12-23.** Prominent structures A, B, C, F, G, and H present in DAB-dendr-(NH<sub>2</sub>)<sub>64</sub>. See Fig. 12-19 for the full (deconvoluted) spectrum of DAB-dendr-(NH<sub>2</sub>)<sub>64</sub>. More details can be found in Table 12-1 where the formulas are explained.

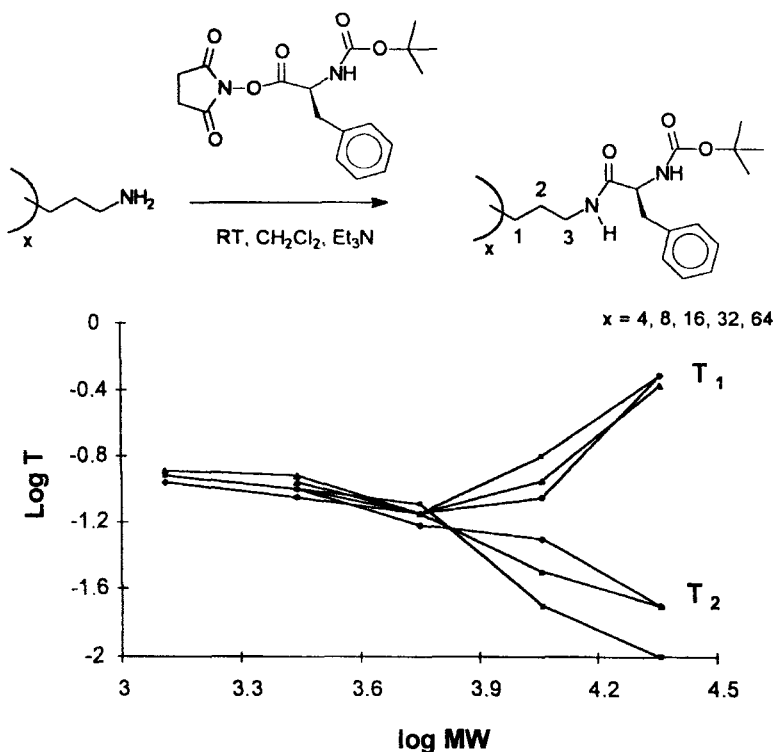
### *The Functionalization of Poly(propylene imine) Dendrimers*

#### *(1) The Dendritic Box*

Modification of the outer amine functionalities of DAB-dendr-(NH<sub>2</sub>)<sub>64</sub> with bulky substituents – typically, *t*-BOC protected L-phenylalanine (*t*-BOC-L-Phe) is used – results in the formation of a structure with a solid shell and a flexible core (Jansen et al., 1996a). Evidence for this framework has been found in spin lattice relaxation measurements (*T*<sub>1</sub>) on carbon atoms in the shell (see Fig. 12-24). *T*<sub>1</sub> increases after the third generation, indicating a decrease in molecular motion. Further evidence for the close packing of the outer layer is found in a combination of chiroptical data and <sup>1</sup>H NMR data. Specific optical rotations reduce to zero on going from DAB-dendr-(NH-*t*-BOC-L-Phe)<sub>4</sub> to DAB-dendr-(NH-*t*-BOC-L-Phe)<sub>64</sub>. This behavior may be rationalized by assuming frozen-in conformations of the L-Phe moieties in the shell of

DAB-dendr-(NH-*t*-BOC-L-Phe)<sub>64</sub>, leading to internal compensation of the optical activity (Peerlings and Meijer, 1997). Indeed, <sup>1</sup>H NMR data show that intramolecular hydrogen bonding interactions between the *t*-BOC-L-Phe moieties are stronger in the higher generation poly(propylene imine) DAB dendrimers, and therefore it is believed that these hydrogen bonds add to the solid phase character of the shell.

The soft-core, hard-shell framework of modified poly(propylene imine) dendrimers has also been named the ‘dendrimer box’ structure, since it can trap small molecules in the cavities of its core (Jansen et al., 1994). The encapsulation of molecules is performed by reaction of DAB-dendr-(NH<sub>2</sub>)<sub>64</sub> with an activated ester of *t*-BOC-L-Phe in the presence of guest molecules with some affinity for the tertiary amine functions in the interior of the dendrimer. Excess guest molecules and molecules adhered to the surface of the box can conveniently be removed by a dialysis procedure. Lower



**Figure 12-24.** Top: the synthesis of a poly(propylene imine) dendrimer with a shell (for  $x=64$ , a 'dendritic box' is created). Bottom: double logarithmic plot of the relaxation data ( $T_1$  and  $T_2$ ) of the carbon atoms 1, 2, and 3 versus the molecular weight (generation) of the inspected dendrimers. The data have been recorded at 75 MHz in  $\text{CDCl}_3$ .

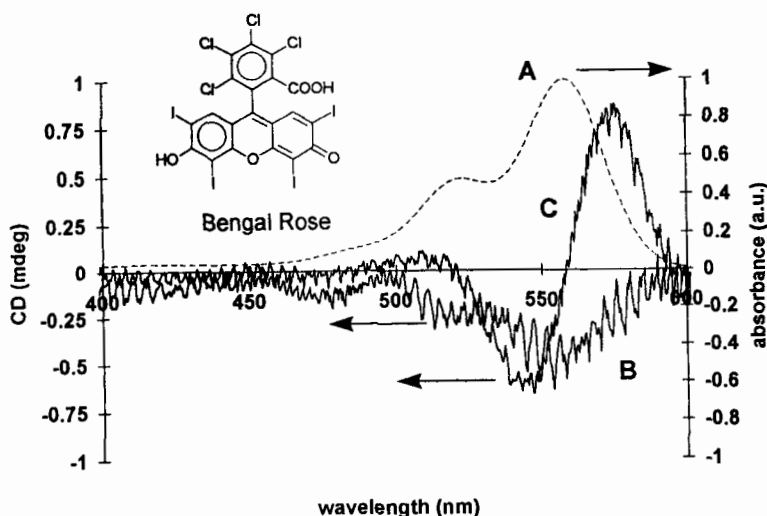
generation poly(propylene imine) dendrimers cannot be used as boxes, since the shells in these systems are not dense enough to capture guest molecules: Dialysis will release all adhered molecules. The encapsulation of dye molecules in general and of Rose Bengal in particular has been studied in detail (Jansen and Meijer, 1996b). The features of these molecules can change upon capturing, obviously as a result of the changed micro-environment. For example, Rose Bengal@DAB-dendr-(NH-*t*-BOC-L-Phe)<sub>64</sub><sup>8</sup> displays strong fluorescence at  $\lambda_{\text{max}}=600$  nm, whereas the fluorescence of free Rose Bengal is quenched in this wavelength region. Induced chirality upon encapsulation has also been found for Rose Bengal. When one molecule of Rose Bengal, an

achiral compound, is trapped, a CD spectrum similar to the UV spectrum is found (see Fig. 12-25). When four molecules are trapped, however, an exciton-coupled Cotton effect is observed, indicating the close proximity of chromophores with a certain fixed orientation. Therefore the cavities in the dendritic box must have retained some chiral features, although the shells of the box do not display any optical activity.

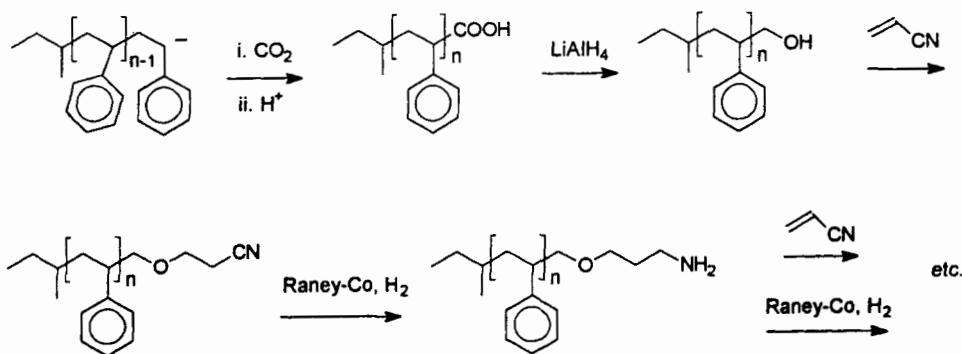
## (2) Amphiphilic Architectures

The acrylonitrile-based dendrimers can also be used to produce new amphiphilic architectures. In one approach, such dendrimers have been grown from an amine functionalized polystyrene (PS) core (see Fig. 12-26) (Van Hest et al., 1995 a). The PS chain is produced by "living" anionic polymerization, so that well-defined molecular weight material is obtained. The amine

<sup>8</sup> Encapsulated species are specified by the @ symbol.



**Figure 12-25.** UV (A) and CD spectra of Bengal Rose@DAB-dendr-(NH-*t*-BOC-L-Phe)<sub>64</sub> containing 1 (B) and 4 (C) molecules of Bengal Rose.

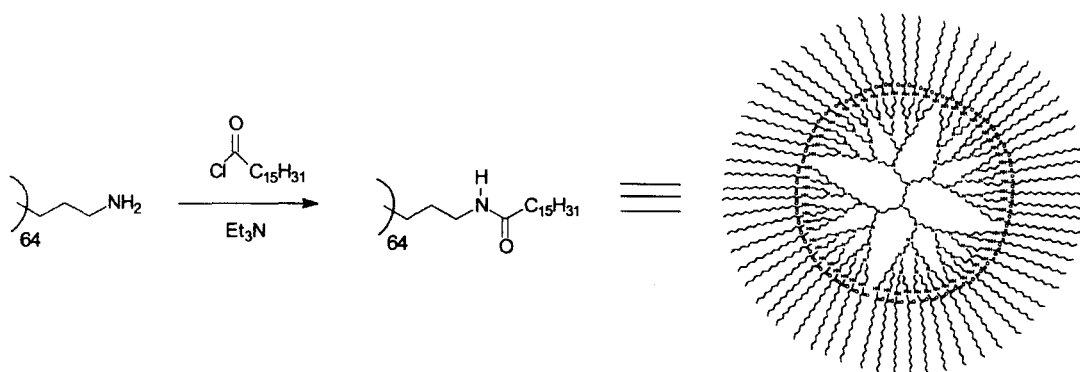


**Figure 12-26.** Modification of ‘living’ polystyrene in order to introduce a primary amine which can function as a core for the poly(propylene imine) dendrimer synthesis.

functionality can be incorporated by subsequent quenching of the “living” atactic PS chain with  $\text{CO}_2$ , reduction of the resulting carboxylic acid with  $\text{LiAlH}_4$ , cyanoethylation of the alcohol with acrylonitrile, and hydrogenation of the nitrile moiety with a Raney-cobalt catalyst. Starting with the PS- $\text{NH}_2$  core and applying the usual sequence of cyanoethylation and reduction steps, PS-dendr-( $\text{NH}_2$ )<sub>x</sub> dendrimers of various generations can be produced. The PS chains in these systems are hydrophobic, whereas the

dendritic head group is hydrophilic; thus nanometric equivalents of surfactant molecules are created. It is possible to produce a broad range of amphiphiles in this class of materials, because the size and nature of the dendritic head group can be varied. The size of the head group can be varied by adjusting the generation of the dendrimer, whereas the nature of the head group can be changed by hydrolyzing PS-dendr-( $\text{CN}$ )<sub>x</sub> to the corresponding carboxylic acid dendrimers (Van Hest et al., 1995 b) or by modify-





**Figure 12-27.** The production of dendritic unimolecular inverted micelles from DAB-dendr- $(\text{NH}_2)_{64}$  and palmitoyl chloride.

ing PS-dendr- $(\text{NH}_2)_x$  with MeI to the fully quaternized products (Elissen-Román et al., 1997).

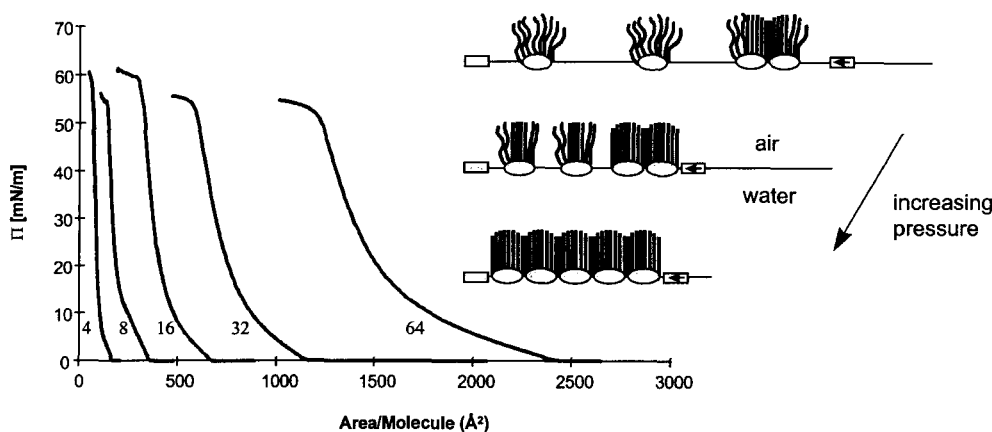
Aqueous solutions of the PS-dendr- $(\text{NH}_2)_x$  amphiphiles have been subjected to conductivity measurements, monolayer experiments, pyrene probe fluorescence experiments, dynamic light scattering (DLS) measurements, and TEM measurements (Van Hest et al., 1996). These characterization techniques have shown that the aggregation behavior of the amphiphiles depends on the size of the head group. As the head group becomes bulkier, the aggregates change their shape from inverted micelles, to vesicles and rod-like structures, and finally to spherical micelles. These observations are in line with Israelachvili's theory on the assembly of surfactant molecules (Israelachvili et al., 1976). In this theory, it is argued that the geometry of the surfactants determines the morphology of their aggregates.

Unimolecular dendritic inverted micelles based on poly(propylene imine) dendrimers can be synthesized by functionalizing DAB-dendr- $(\text{NH}_2)_x$  materials with long alkyl chains [DAB-dendr- $(\text{NHCOC}_{5,9,15})_{8-64}$  materials have been produced<sup>9</sup>, see Fig. 12-27]. The reaction is executed using alkyl

acid chlorides, applying THF or  $\text{CH}_2\text{Cl}_2$  as the medium and using  $\text{Et}_3\text{N}$  as the HCl scavenger (Stevelmans et al., 1996). Remarkably, two compounds are isolated when an excess of DAB-dendr- $(\text{NH}_2)_x$  dendrimer is used, i.e., the totally modified and completely unmodified product. Apparently, a partly alkylated product has a dramatically increased reactivity towards alkylation.

As observed for the dendritic box, the unimolecular inverted micelle is able to capture guest molecules such as dyes. The hydrophilic dye is trapped into the micelle by dissolving the micelle and the dye in ethanol with the subsequent precipitation of the mixture in acetonitrile. Excess and adhered Rose Bengal is removed by extensive washing or dialysis with acetonitrile and water. The number of trapped dye molecules in the Rose Bengal@DAB-dendr- $(\text{NHCOC}_{5,9,15})_{8-64}$  systems<sup>8</sup> can be determined by UV spectroscopy in ethanol, and varies between one and seven molecules per micelle. This number depends on both the length of the alkyl chain and the generation of the dendrimer. The unimolecular invert-

<sup>9</sup> In the formulae for these dendrimer based unimolecular inverted micelles, the length of the alkyl chains is indicated.



**Figure 12-28.** Monolayer experiments on palmitoyl-derivatized poly(propylene imine) DAB dendrimers. Graph: compression isotherms of different generation materials on  $\text{H}_2\text{O}$  at  $25^\circ\text{C}$ . The indicated numbers refer to the amount of palmitoyl chains in the unimolecular micelle. Inset: schematic representation of the organization of the inverted micelles in a monolayer. Upon compression, the alkyl chains adopt an all-trans conformation. The cross-sectional area of a palmitoyl chain in an all-trans conformation is  $25 \text{ \AA}^2$  ( $0.25 \text{ nm}^2$ ).

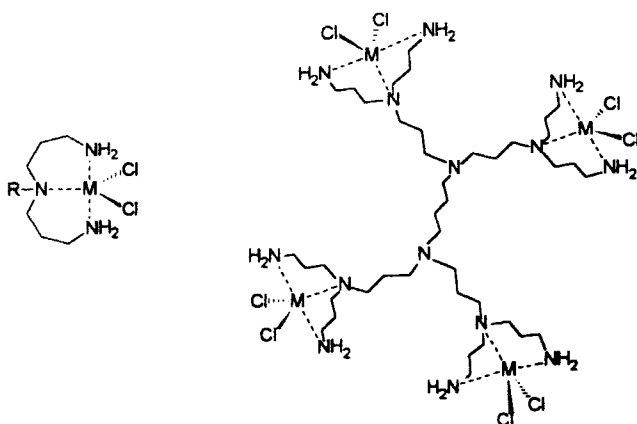
ed micelle is a dynamic host system, since the host can release the trapped molecules by dissolving the host–guest micelle in the appropriate solvent. The trapping qualities, i.e., the extractant qualities, of DAB-*dendr*-( $\text{NHCOC}_{15}$ )<sub>64</sub> have been used in liquid–liquid extractions of various anionic dye solutes, including Rose Bengal (Baars et al., 1997). The extraction behavior is clearly related to the tertiary amine interior of the dendrimer, and under optimum extraction conditions up to 50 (!) Rose Bengal molecules can be extracted by one DAB-*dendr*-( $\text{NHCOC}_{15}$ )<sub>64</sub> molecule.

The DAB-*dendr*-( $\text{NHCOC}_{5,9,15}$ )<sub>8–64</sub> components can be investigated with monolayer experiments (Schenning et al., 1998). The inverted micellar structures of, for example, DAB-*dendr*-( $\text{NHCOC}_{15}$ )<sub>64</sub>, is converted to a structure similar to traditional head–tail surfactant structures when this component is layered on a water surface (see Fig. 12-28). Apparently, even this high generation functionalized dendrimer is flexible enough to adjust its conformation, given the experimental conditions. Latterman (Came-

ron et al., 1997) has shown another example of the conformational flexibility of poly(propylene imine) dendrimers by functionalizing these dendrimers with mesogenic groups (i.e., 3,4-alkoxy benzoyl chloride). Thermotropic LC materials are obtained in which the dendritic parts are forced to stack in hexagonally packed columns.

### (3) Metallodendrimers

The DAB-*dendr*-( $\text{NH}_2$ )<sub>x</sub> materials contain bis(3-aminopropyl)amine tridentate coordination sites which have a strong affinity for various transition metals, such as Cu(II), Zn(II), and Ni(II) [see Fig. 12-29 (Bosman et al., 1997)]. Indeed, UV titration data show that DAB-*dendr*-( $\text{NH}_2$ )<sub>x</sub> dendrimers give a complex in methanol with exactly  $x/2$  units of  $\text{CuCl}_2$  or  $\text{ZnCl}_2$ . TEM data reveal spherical structures with the anticipated dimensions, indicating that unimolecular nanoscopic structures are formed. Further investigation in this area may lead to the use of these or similar metallodendrimers as catalysts.



**Figure 12-29.** Tridentate complexation of the bis(3-aminopropyl)amine moiety with transition metal chlorides. As an example, the complex with DAB-*dendr*-(NH<sub>2</sub>)<sub>8</sub> is shown.

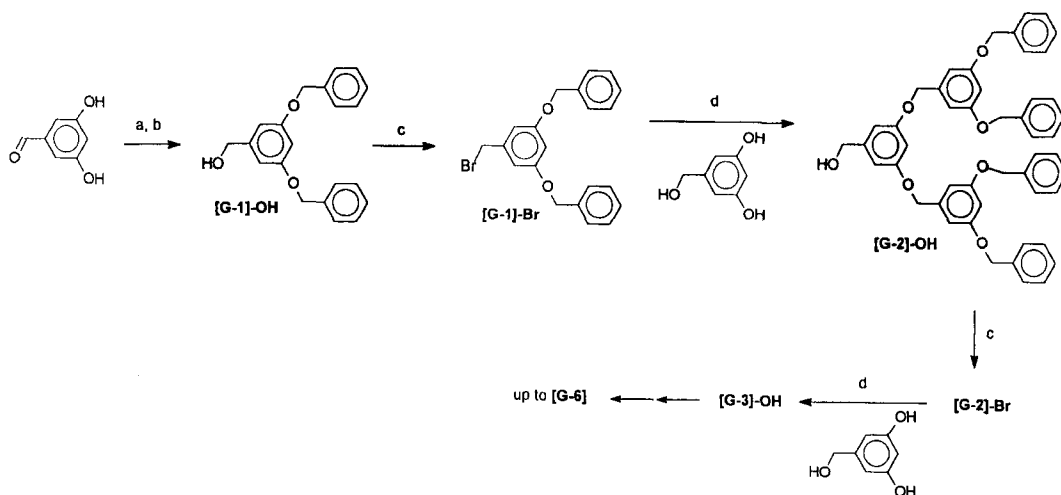
## 12.2.2 Convergent Methods

### 12.2.2.1 Fréchet's Polyether Dendrimers

The Fréchet-type dendrimers are produced in a repeat of an activation step and an expansion step using 3,5-dihydroxybenzyl alcohol as the building block (see Fig. 12-30) (Hawker and Fréchet, 1990). In this way, so-called 'wedges', 'dendrons', or 'monodendrons' are synthesized. These wedges can be connected to a multifunctional core molecule to produce 'multidendron' dendrimers. The synthetic procedure is started by protecting 3,5-dihydroxybenzaldehyde with benzyl bromide and reducing the product to the corresponding benzyl alcohol (the direct benzylation of 3,5-dihydroxybenzyl alcohol results in a C-alkylated product). This first generation alcohol [G-1]-OH is activated by bromination. In the actual growth step, two bromide molecules [G-1]-Br are reacted with one unit of 3,5-dihydroxybenzyl alcohol to produce the next generation dendrimer [G-2]-OH. The activation and expansion steps can be repeated to produce higher generation wedges and, finally, activated wedges of generation  $G_n$  can be coupled to, for example,

a 1,1,1-tris(4'-hydroxyphenyl)ethane core molecule, resulting in a 'tridendron' of generation  $G_n$  denoted as [G- $x$ ]<sub>3</sub>-[C]. Dendrimers up to generation  $G_6$  have been reported and, apart from the first two generations, all the materials are isolated as colorless glasses.

The two steps in the production of polyether dendrimers, i.e., the coupling-growth step and the bromination-activation step, have been optimized in order to avoid complicated purification procedures (Hawker and Fréchet, 1990). Reaction conditions for the bromination-activation step comprise the use of CBr<sub>4</sub> and PPh<sub>3</sub> in minimum amounts of THF as the solvent. As higher generation dendrimers are produced, larger excesses of CBr<sub>4</sub> and PPh<sub>3</sub> are required and isolated yields decline. The coupling-growth step has been optimized by studying the synthesis of the first generation alcohol [G-1]-OH: A Williamson synthesis of a phenol with a bromide. A variety of solvent-base combinations have been scanned and, additionally, the use of phase transfer agents has been investigated. Optimum reaction conditions involve the use of K<sub>2</sub>CO<sub>3</sub> as the base, acetone as the solvent (reflux conditions), and 18-crown-6 as the phase transfer catalyst. Under these conditions, O-alkyla-



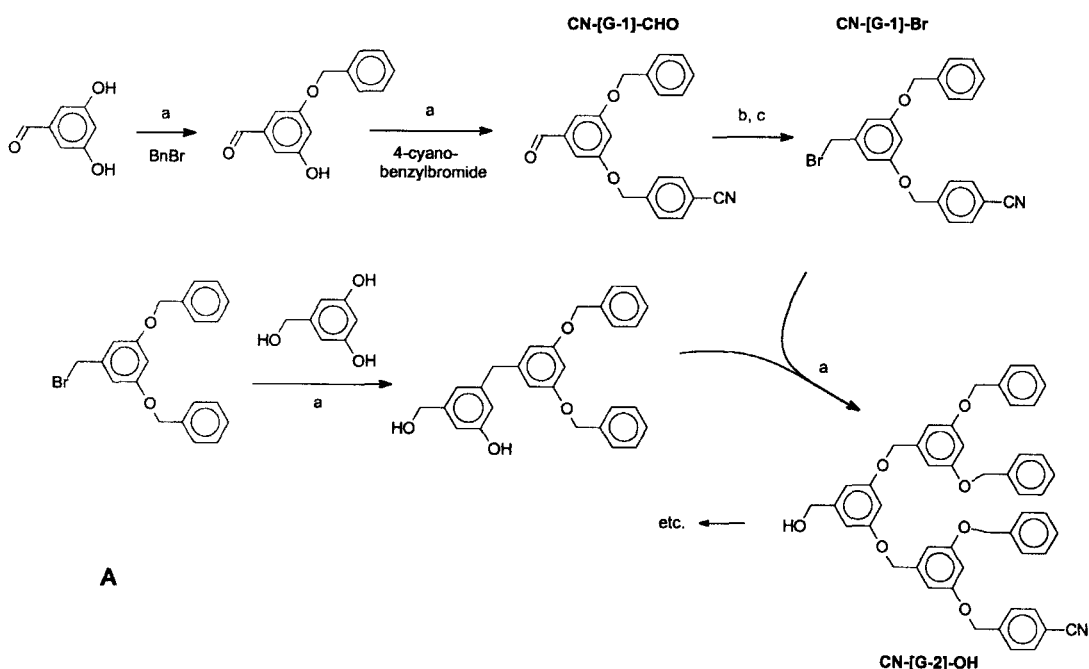
**Figure 12-30.** Preparation of Fréchet-type dendrimers: a)  $\text{BnBr}$ ,  $\text{K}_2\text{CO}_3$ , 18-crown-6, acetone; b)  $\text{NBu}_4\text{BH}_4$ ; c)  $\text{CBr}_4$ ,  $\text{PPh}_3$ , THF; d)  $\text{K}_2\text{CO}_3$ , 18-crown-6, acetone.

tion is promoted and C-alkylation is prohibited: a result that is crucial for the success of this dendrimer synthesis. Furthermore, vigorous stirring and prolonged reaction times of typically 48 h have been applied to secure maximum yields in this growth step. The reaction of activated wedges with a multiphenolic core is also executed by applying the mentioned conditions for a Williamson synthesis. For both the activation step and the expansion step, lower yields were observed as higher generation material was produced, indicating that the functional group located at the focal point of the wedge is reduced in activity as a result of steric congestion.

The synthesis of structural variations on the Fréchet-type dendrimers is facilitated by the convergent approach towards these dendrimers. For example, it is possible to introduce a discrete number of functional groups at the periphery of a dendron by coupling monofunctionalized 3,5-dihydroxybenzyl alcohol to an unsymmetrical wedge (see Fig. 12-31 A) (Wooley et al., 1991). In this manner, a new unsymmetrical wedge is pro-

duced which can be used to synthesize the next generation dendrimer with a single functional group at the periphery. The functional group can be used for modification purposes (Wooley and Fréchet, 1992). In another structural variation of the Fréchet-type dendrimers, a difunctional core molecule is sequentially linked to two dendrons of opposing polarity (Sanford et al., 1993). Such a strategy produces dendritic molecules with an amphiphilic character (see Fig. 12-31 B).

Fréchet-type polyether dendrimers can also be used to produce block copolymers. ABA-type or AB-type block copolymers have been described consisting of dendron A-blocks and linear macromolecule B-blocks. Polyethylene oxide (PEO) (Gitsov and Fréchet, 1993) as well as polystyrene (PS) (Gitsov and Fréchet, 1994) have been used as linear components. The synthesis of ABA-type block copolymers containing a PEO central block has been achieved by a Williamson synthesis of PEO with dendritic bromides (such as, for example,  $[\text{G}-4]\text{-Br}$ ). In an alternative synthesis, dendrons



**Figure 12-31.** Modifications of Fréchet-type dendrimers. A) The synthesis of dendrimers with one cyano function at the periphery: a)  $K_2CO_3$ , 18-crown-6, acetone; b)  $NBu_4BH_4$ ; c)  $CBr_4$ ,  $PPh_3$ , THF. B) The production of amphiphilic dendrimers using two wedges with surface functionalities of opposing polarity.

with methyl ester focal points have been subjected to transesterification with PEO. Remarkably, the reaction rate for the Williamson synthesis *increases* with the length of the PEO block or the generation of the dendron, a result that is not well understood. The PEO-based block copolymers display amphiphilic behavior. In methanol–water solvent mixtures, micelles with hydrophobic dendron cores and hydrophilic PEO shells are formed. In the solid state, the block copolymers exhibit phase separation, resulting in the observation of two glass transition temperatures. The PS-based block copolymers have been produced by treating ‘living’ PS with 1,1-diphenylethylene and quenching the resulting anion with a dendritic bromide or aldehyde. By choosing a difunctional initiator in the ‘living’ polymerization, ABA-type block copolymers can be created. DSC measurements on

the ABA block copolymers bearing a PS central block have shown a single glass transition temperature, indicating that both blocks are molecularly miscible. In contrast, physical mixtures of the two individual components do not mix and phase separate.

In the previous paragraphs, examples of controlled molecular architectures have been described in which the Fréchet-type dendrons have been incorporated. Many such architectures have been reported by Fréchet’s group as well as by other authors (Jin et al., 1993; Schlüter, 1995), showing that the polyether dendrimers are relatively easily accessible. For instance, Schlüter (Schlüter, 1995; Claussen et al., 1995; Freudenberger et al., 1994) has reported the synthesis of cylindrically shaped polymers in which small polyether wedges have been attached to polyphenylene or poly([1.1.1]propellane) backbones (see Fig. 12-32). In an-

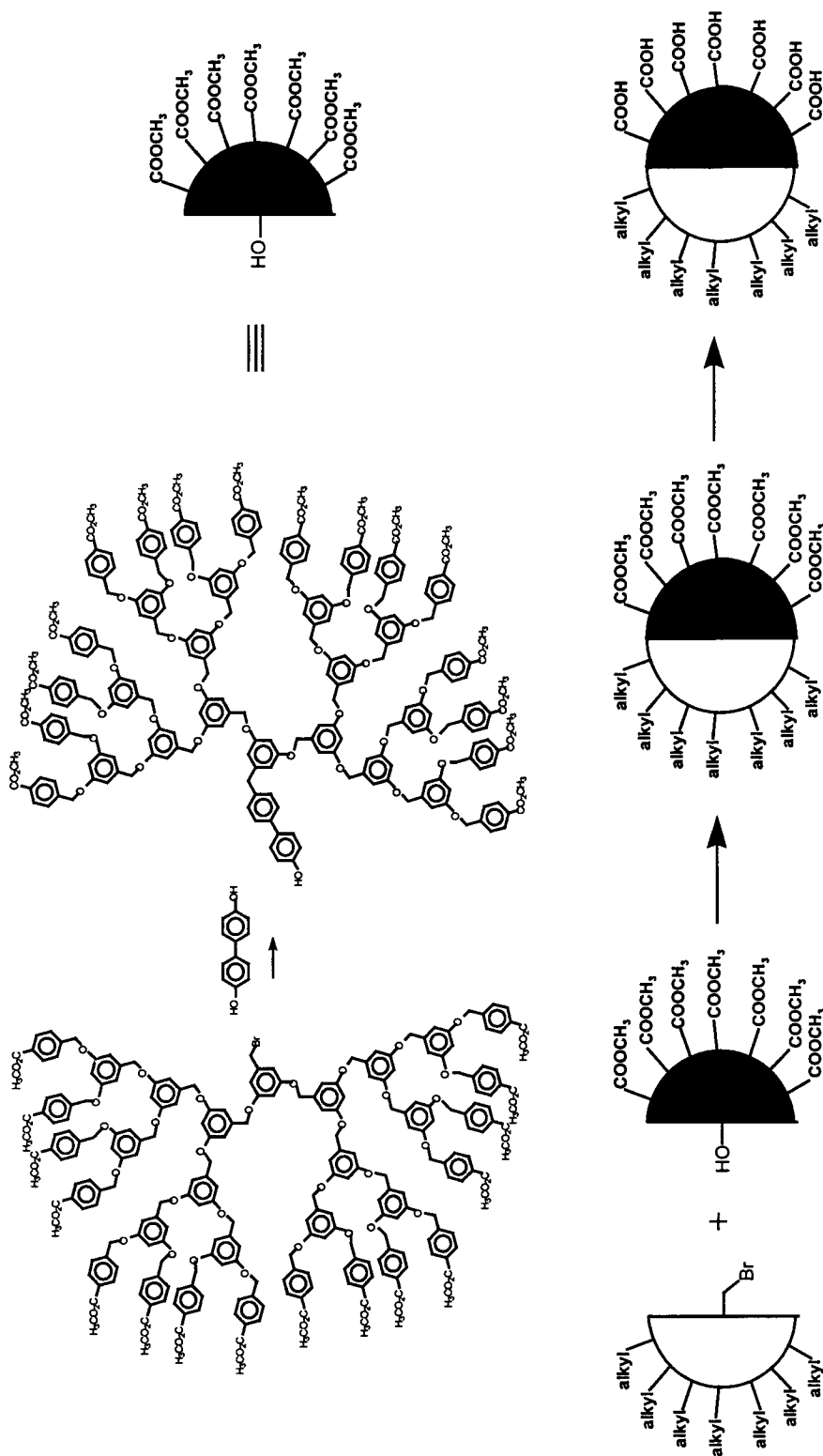
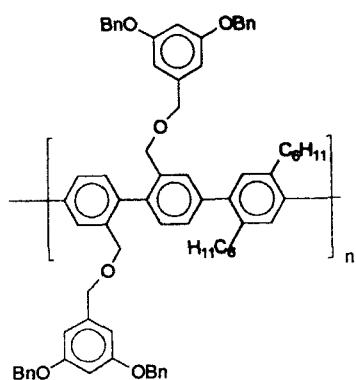


Figure 12-31. B



**Figure 12-32.** An example of Schlüter's cylindrically shaped rigid rods. Polyether wedges of the first generation are attached to a polyphenylene backbone.

other example by Kremers and Meijer (1994), pentaerythritol has been modified with four polyether wedges, each of a different generation. The racemic product could not be separated into its enantiomers, nor could enantioselective recognition be induced by chiral auxiliaries.

The polyether dendrimers produced by Fréchet have been analyzed using a broad range of characterization techniques including NMR spectroscopy (Hawker and Fréchet, 1990), SEC (Hawker and Fréchet, 1990), DSC measurements (Wooley et al., 1993), and intrinsic viscosity measurements (Mouray et al., 1992). Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry (Leon and Fréchet, 1995) has been applied to investigate the presence of structurally related impurities, since spectroscopic techniques are not capable of detecting such species. Scanning various matrices, it has been possible to analyze higher generation material, showing that the experimental molecular weights corresponded well with the calculated molecular weights. Even for dendrons of generation  $G_6$ , very limited amounts of impurities have been detected, proving the integrity of the convergent synthesis of the

Fréchet-type dendrimers. Unfortunately, MALDI-TOF mass spectrometry does not allow for an in-depth qualitative and quantitative analysis of impurities in a homologous series of dendrimers, since not all dendritic materials can be 'taught to fly' (i.e., a suitable matrix cannot be found for all dendrimers).

DSC data (Wooley et al., 1993) show that the glass transition temperature ( $T_g$ ) of polybenzylether dendrimers correlates to  $n_e/M$  ( $n_e$  is the number of chain ends and  $M$  is the molecular weight of the dendrimer). This result shows that the traditional relationship between the  $T_g$  value of a linear polymer and its molecular weight  $M$  – this relationship is based on the chain end free volume theory – can be modified to account for the special architecture of dendritic macromolecules. Furthermore, it has been shown that an increasing polarity of the chain end functionalities largely increases the  $T_g$  value of the dendrimer. In conclusion, tailoring of the glass transition temperature  $T_g$  is possible for Fréchet-type dendrimers.

Intrinsic viscosity measurements (Mouray et al., 1992) on the polybenzylether dendrimers confirm the unique behavior of dendritic molecules: At a certain generation the increase of the intrinsic viscosity stops and the onset of a viscosity decline is reached. The viscosity drop can be explained, not only by the previously mentioned model proposed by de Gennes (de Gennes and Hervet, 1983), but also by an alternative model proposed by Lescanec (Lescanec and Muthukumar, 1990). As opposed to the model of de Gennes, in which a density maximum is predicted at the periphery of the dendrimer, this alternative model predicts a density maximum at the core (as a result of the inward folding of branch units). It should be mentioned, however, that the radial distribution of terminal groups in dendrimers remains a subject of debate (Mansfield and

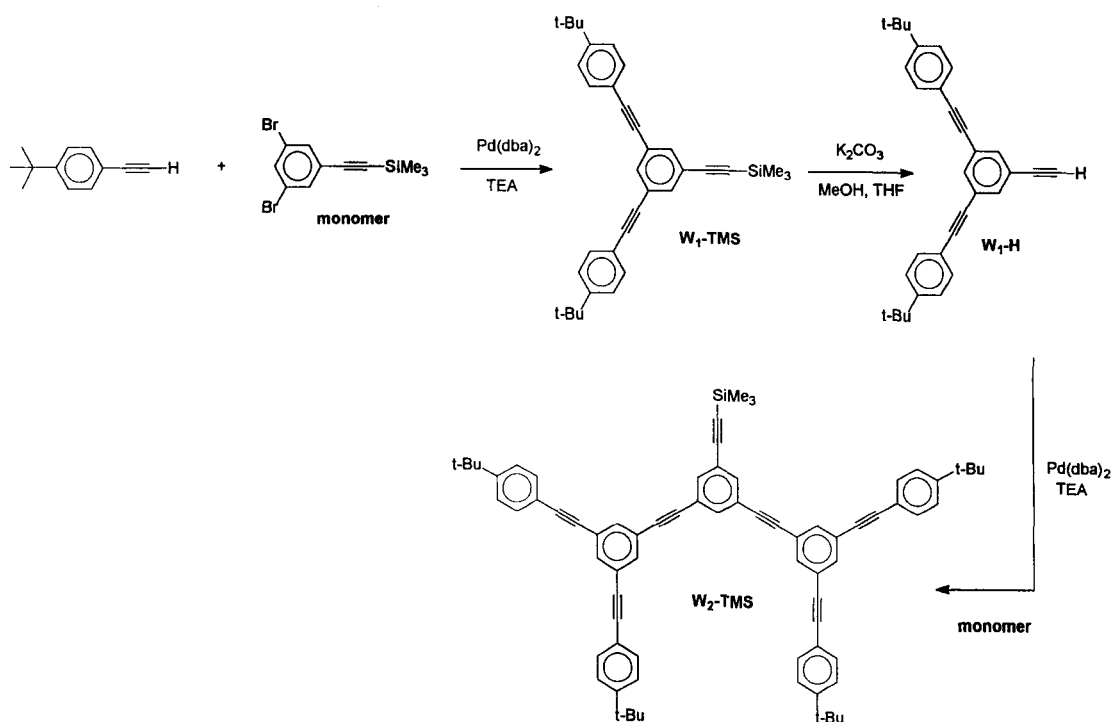
Klushin, 1993) and cannot be derived from intrinsic viscosity measurements alone. Furthermore, it can be argued that this distribution of terminal groups is conditioned by the experimental circumstances and by possible secondary interactions (such as H-bonding) within the shell of the dendrimer (Bosman, 1998).

### 12.2.2.2 Hydrocarbon Dendrimers

Strictly hydrocarbon, phenylacetylene dendrimers (PADs) have been reported by Moore et al. The rigidity in the phenylacetylene units of these dendrimers results in a three-dimensional structure that is more defined than for other dendritic systems, which have usually been constructed from flexible units. The initial strategy in the con-

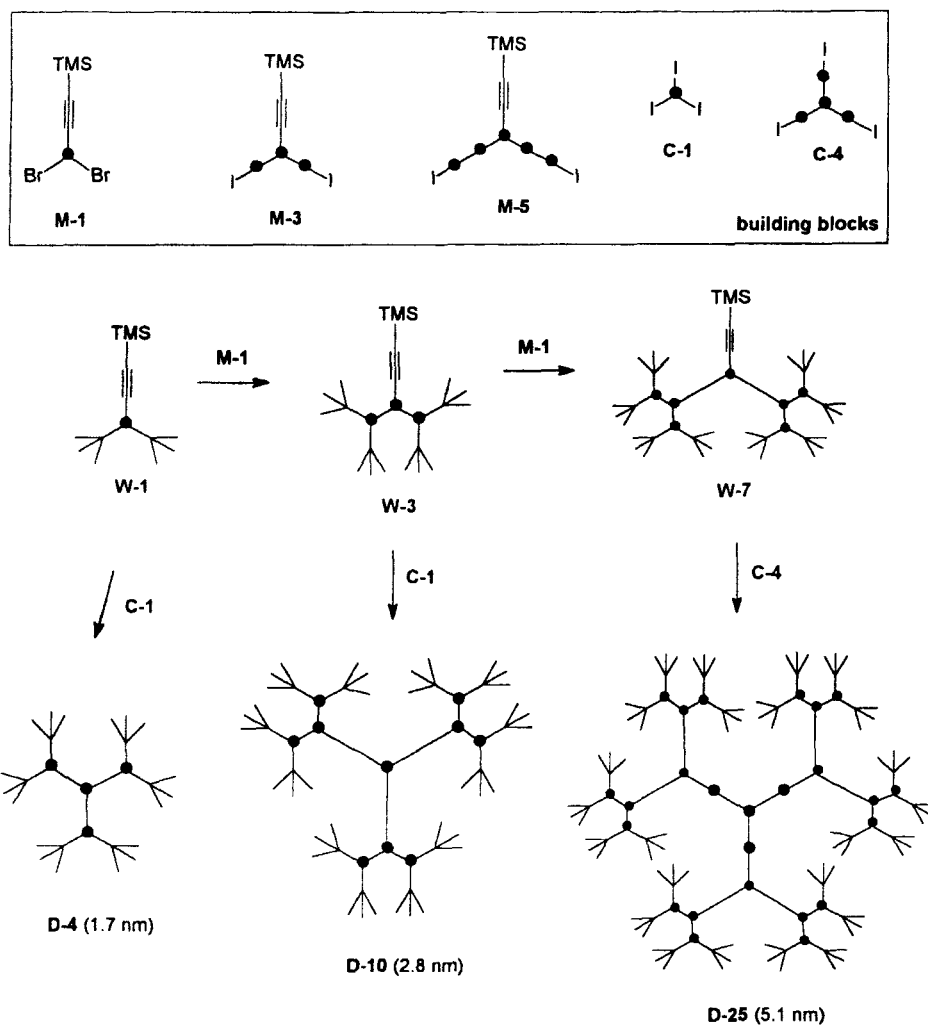
struction of phenylacetylene-based dendrimers uses trimethyl silyl protected 1-ethynyl-3,5-dibromobenzene as the building block (Moore and Xu, 1991a). The production of dendritic material is accomplished by a repetitive sequence of a palladium-catalyzed cross coupling reaction and deprotection of a trimethylsilyl masking group (see Fig. 12-33). Unfortunately, this strictly convergent approach has proven to be useful only up to generation  $G_3$  (15 benzene units). Further growth is inhibited by crowding around the active acetylene and bromide centers in this third-generation dendron.

Alternatively, the phenylacetylene-based dendrimers have also been produced using a set of building blocks consisting of monomers (**M-x**), cores (**C-x**) and wedges (**W-x**) with various numbers of benzene



**Figure 12-33.** The first published convergent strategy towards phenylacetylene dendrimers;  $\text{SiMe}_3$  protected 1-ethynyl-3,5-dibromobenzene is used as the monomer. **W<sub>2</sub>-TMS** denotes a second generation wedge with a TMS focal point. In later publications, 3,5-di-*tert*-butyl benzene instead of 4-*tert*-butyl benzene is used as the peripheral group.



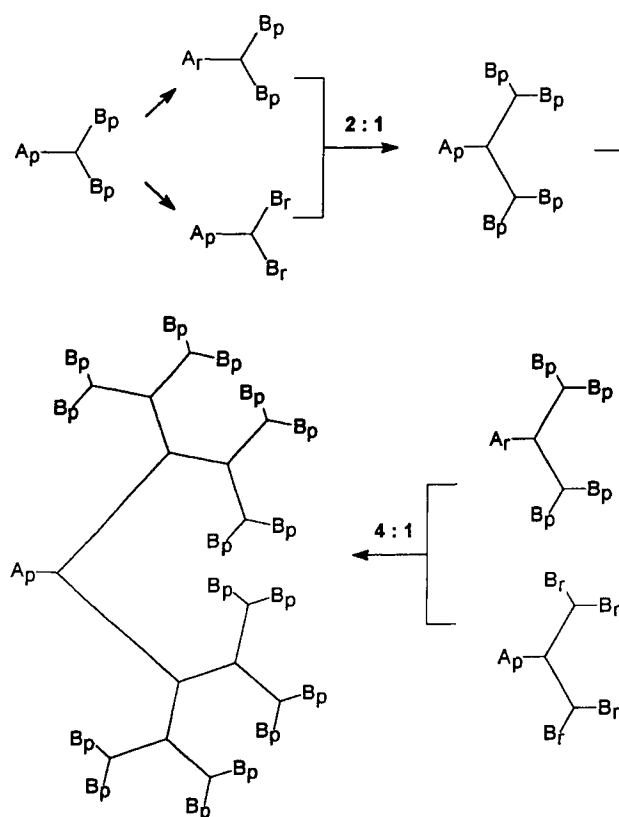


**Figure 12-34.** The preparation of phenylacetylene dendrimers (PADs) using various building blocks (monomers **M**, wedges **W**, and cores **C**). This specific convergent technique, in which the size of the core scales with the size of the wedges, has led to dendrimers with up to 127 benzene units (**D-127**). Symbols: ● = 1,3,5-substituted or 1,4-substituted phenyl ring; line = acetylene unit; TMS = trimethylsilyl group; cross = *tert*-butyl group. The dimensions of the dendrimers are shown in brackets.

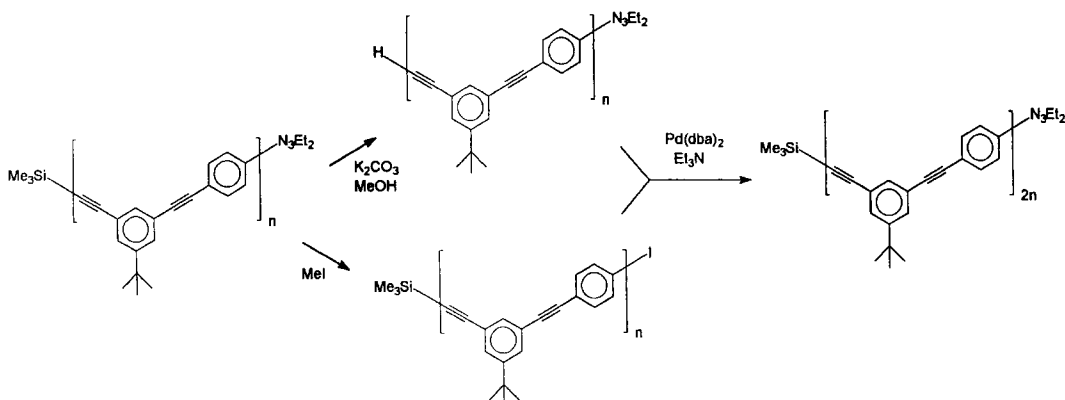
units ( $x$ ) (Xu and Moore, 1993; Xu et al., 1994). By combining the monomers with the appropriate cores and wedges, the synthesis of a wide variety of dendrimers (**D- $x$** ) is facilitated. Using this approach, crowding around the active acetylene moieties in larger monomers is compensated for by using larger cores with easily accessible aryl iodide active centers. In Fig. 12-34, a set of

monomers and cores (**M- $x$**  and **C- $x$** ) and the acquired dendrimers (**D- $x$** ) are shown. Molecular modeling has shown that **D-127** (not displayed) is a dendrimer with a diameter of approximately 12.5 nm.

Finally, PADs can also be synthesized by the so-called 'double exponential growth' technique (see Fig. 12-35) (Kawaguchi et al., 1995). Essentially, this technique



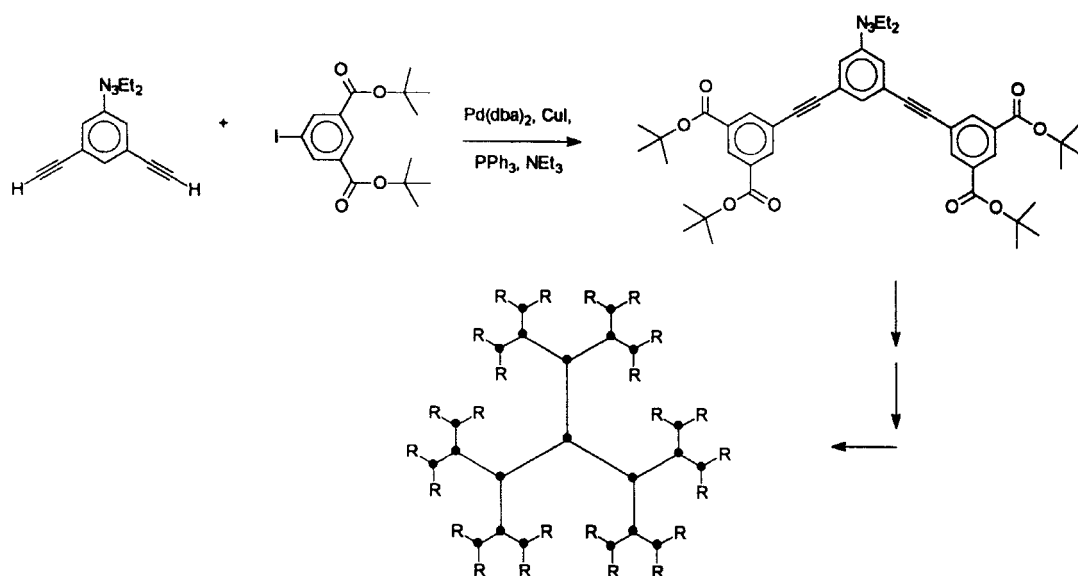
**Figure 12-35.** The 'double exponential growth' construction of phenylacetylene dendrimers. Group A is the focal point and group B is the peripheral group. Both groups can be inactive (protected groups  $A_p$  or  $B_p$ ) or reactive ( $A_r$  or  $B_r$ ). Generation  $n$  has  $2$  raised to the power  $2^{n-1}$   $B_p$  groups.



**Figure 12-36.** The synthesis of linear phenylacetylenes. The use of orthogonal masking groups and high yield deprotection and coupling reactions facilitates the preparation of oligomers of considerable length (up to  $n=4$ ).

combines features of both the divergent and the convergent approach towards dendrimers. Rapid synthesis of a dendron with up to 255 benzene units is feasible when the double exponential growth technique is used.

The chemistry that has been used in the activation and coupling of dendritic phenylacetylene fragments can be illustrated by discussing the stepwise production of linear phenylacetylenes (see Fig. 12-36) (Zhang

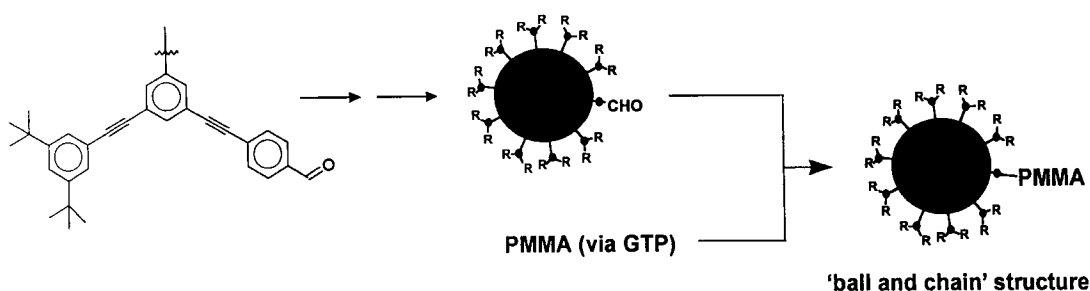


**Figure 12-37.** PADs with *tert*-butyl ester or carboxylic acid groups at the periphery. Symbols: ● = 1,3,5-substituted phenyl ring; line = acetylene unit; R = *tert*-butyl ester or carboxylic acid group.

et al., 1992). One type of coupling method is used: a  $\text{Pd(dba)}_2$  catalyzed cross coupling reaction between a phenylacetylene and an aromatic halide (preferably iodides, bromides are used sometimes). The reaction conditions involve the use of  $\text{CuI}$  and  $\text{PPh}_3$  as co-catalysts and triethylamine as the base and solvent. The coupling reaction must be carried out under oxygen-free conditions and must preferably be conducted at low reaction temperatures; in this manner, unwanted oxidative dimerizations of the acetylene starting compounds can largely be suppressed. Two types of activation reaction have been used; both are deprotection steps. An aryl iodide is introduced by the deprotection of an aryl diethyltriazene with  $\text{MeI}$  (Moore et al., 1991b), and an acetylene moiety is created by deprotection of a trimethylsilyl group. The strength of the iterative synthesis of linear phenylacetylenes lies not only in the high-yield syntheses, but is mainly due to the complementarity of the trimethylsilyl and the diethyltriazene mask-

ing groups. Each masking group can selectively be removed in the presence of the other, and both protecting groups are stable to cross-coupling conditions. Note that the double exponential growth technique illustrated in Fig. 12-35 relies on the use of complementary (or orthogonal) masking groups.

The purity of the isolated dendritic materials has been validated by using thin layer chromatography (TLC), elemental analysis, various NMR spectroscopy techniques, SEC, and mass spectrometry techniques (MALDI-TOF has mainly been used) (Moore and Xu, 1991a; Xu and Moore, 1993; Xu et al., 1994; Kawaguchi et al., 1995; Zhang et al., 1992; Walker et al., 1994). The combination of TLC data, which can be used to recognize the diacetylene side products, and NMR data, which can confirm the exact nature of the isolated product, has shown that the pursued reaction path to the PADs is viable. For higher generation dendrimers, two-dimensional  $^1\text{H}$ , $^1\text{H}$ -COSY and



**Figure 12-38.** Schematic representation of the preparation of a phenylacetylene dendrimer ('ball') attached to a PMMA polymer ('chain').

*J*-resolved NMR data are necessary to prove the constitution of these dendrimers. Additionally, correct mass data on several high molecular weight PADs have been recorded using MALDI-TOF measurements by applying a retinoic acid matrix (Xu et al., 1994; Kawaguchi et al., 1995; Walker et al., 1994). MALDI-TOF mass spectrometry has also been used to optimize the synthesis of the 255-mer via the double exponential growth technique (see Fig. 12-35): Only MALDI-TOF data can indicate incomplete conversion products such as the 240-mer and the 225-mer (Kawaguchi et al., 1995).

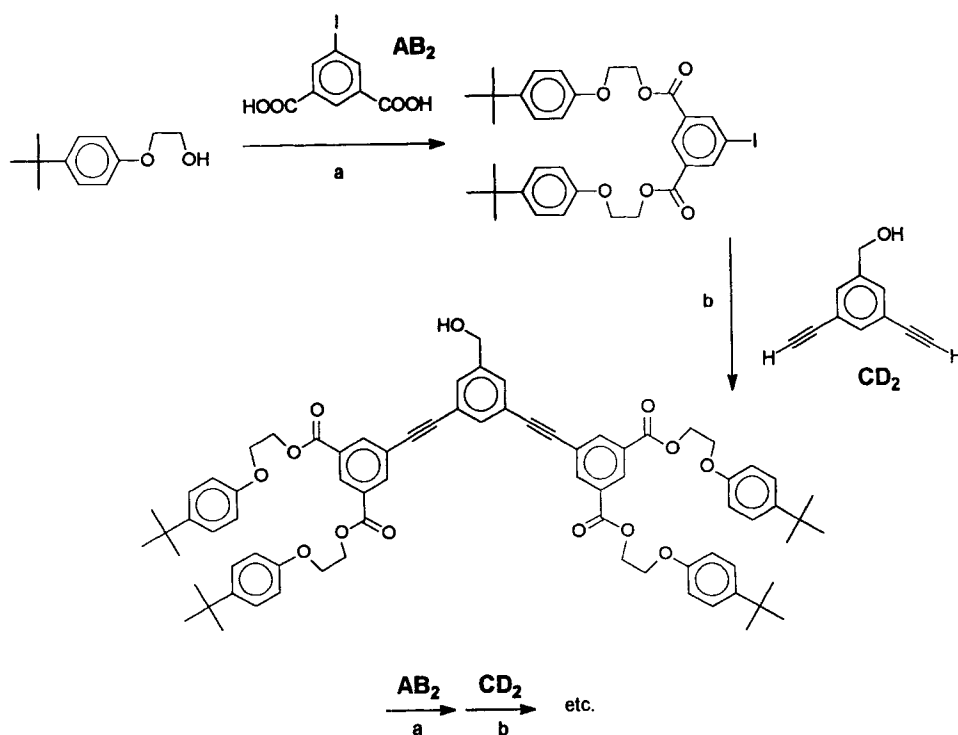
The functional groups at the periphery of the PADs can be varied by initiating the convergent synthesis of these dendrimers with the appropriate aryl iodide. In this fashion, PADs with 3,5-di-*tert*-butyl ester terminal functionalities have been produced (see Fig. 12-37) (Pesak and Moore, 1995). The esters can be hydrolyzed thermally to afford carboxylic acid terminated dendritic molecules. Upon dissolution in basic aqueous solutions these molecules behave as stiff unimolecular micelles.

The PADs have been used for the synthesis of so-called 'ball-and-chain' copolymers (Kawaguchi and Moore, 1994) (DAB dendrimers and Fréchet-type dendrimers have been used to produce similar architec-

tures). The 'ball'-structure is a PAD with one aldehyde functional group at the periphery and is prepared by a synthetic approach similar to Fréchet's strategy towards dendrimers with controlled surface functionality (see Fig. 12-31A): Unsymmetrical dendrons of one generation are used to produce unsymmetrical dendrons of the next generation. The ball-and-chain structure is produced by quenching a group transfer living polymerization of polymethylmethacrylate (PMMA) with a mono-aldehyde PAD (see Fig. 12-38).

Finally, the chemistry used in the synthesis of PADs has been elegantly applied in the production of phenylacetylene macrocycles (PAMs) such as those shown in Fig. 12-39 (Zhang et al., 1994a). The final cyclization involves the palladium-catalyzed internal cross-coupling reaction of an oligomer with an aryl iodide terminus and an acetylene terminus. As a result of the rigidity in the phenylacetylene molecules, the PAMs can be isolated in high yields of typically 70–80%. The pendant chains in the macrocycles can be varied and, for some species in the PAM series, liquid-crystalline behavior has been observed (Zhang and Moore, 1994b). Electron microscopy and diffraction methods confirm the face-to-face stacking of the PAMs in the solid state (Buchko et al., 1995).





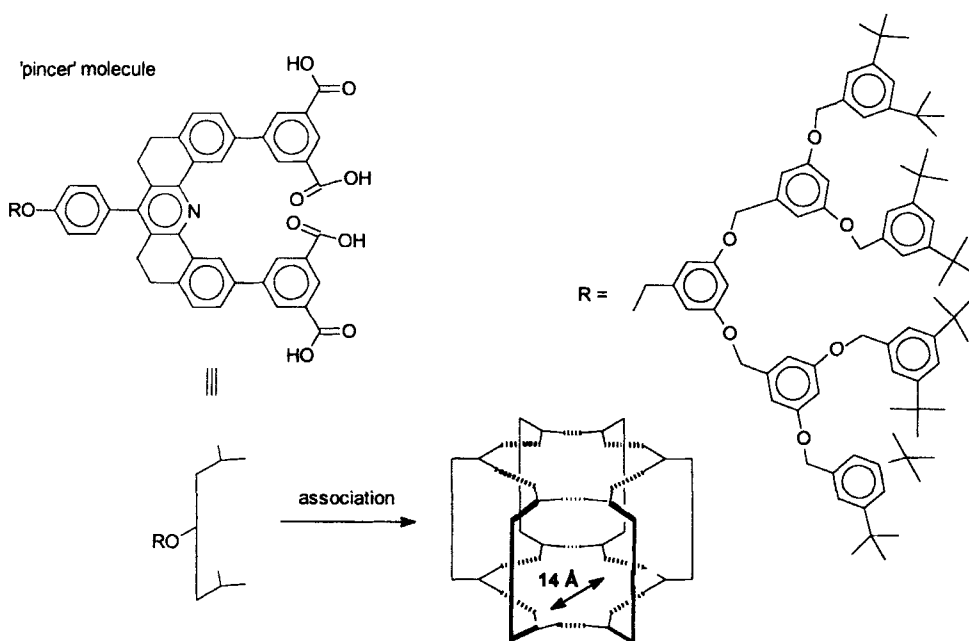
**Figure 12-40.** The orthogonal coupling strategy towards dendrimers as reported by Zimmerman. a)  $PPh_3$ , diethyl azodicarboxylate (DEAD), THF; b)  $Pd(PPh_3)_2Cl_2$ , CuI, or  $Pd_2(dba)_3$ , CuI,  $PPh_3$ ,  $Et_3N$ ,  $PhCH_3$ .

struction of dendrimers was previously demonstrated by, for example, Fréchet (Wooley et al., 1994c).

Zimmerman has also introduced the use of hydrogen bonds in the linking of dendritic substructures (Zimmerman et al., 1996). One of the systems developed by Zimmerman is shown in Fig. 12-41. The depicted 'pincer' molecules, in which a pair of isophthalic acid units are connected via a rigid spacer, can assemble in  $CHCl_3$  to linear oligomers or to a cyclic hexamer. Introduction of a dendritic wedge to the rigid spacer gives the preferential formation of the cyclic hexamer, probably due to the inhibition of the formation of linear structures by crowding. Evidence for the formation of a discrete hexamer has been found by a combination of SEC, VPO, and LLS (laser light scattering)

data. The hexamer contains a void of considerable size [ $d = 14 \text{ \AA}$  (1.4 nm)], and therefore applications in catalysis have been suggested.

Dendritic architectures containing metals have been reported by several authors. Besides the previously discussed (surface) functionalization (Newkome et al., 1994a; Newkome and Moorefield, 1994b; Bosman et al., 1997; Moulines et al., 1993; Liao and Moss, 1993; Alonso et al., 1994; Knapen et al., 1994; Bardaji et al., 1997), metals have also been used as branching points (Bochkarev et al., 1988) and as building block connectors (Achar and Puddephatt, 1994). Balzani and co-workers have reported 2,3-bis(2-pyridyl)pyrazine ligands that are linked by ruthenium or osmium cations to afford well-defined dendritic structures

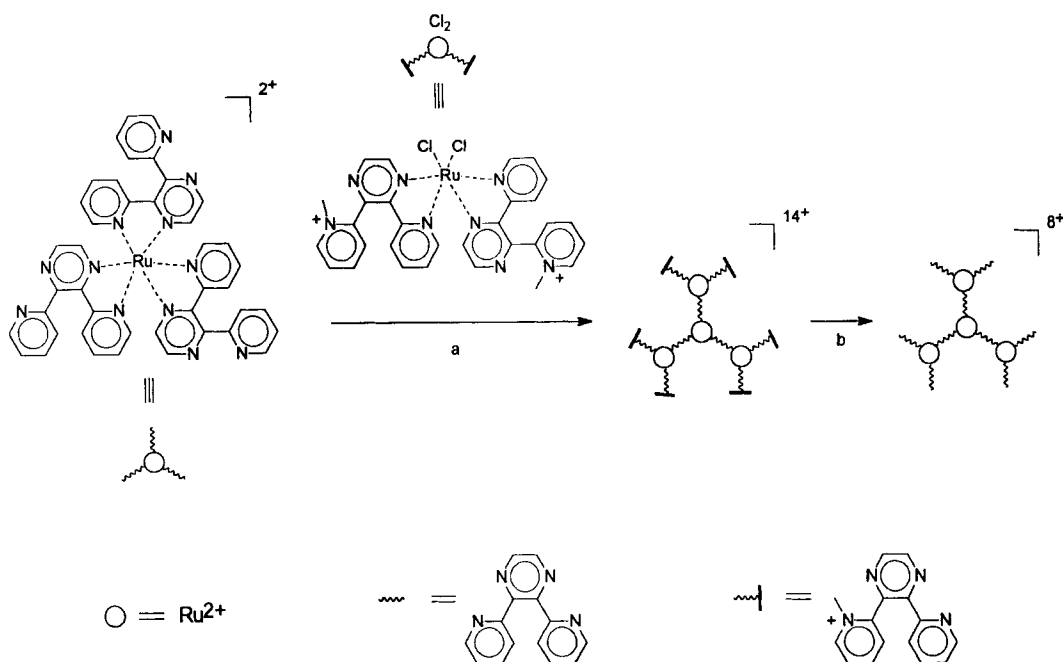


**Figure 12-41.** The 'pincer' molecule developed by Zimmerman bears a rigid spacer with a pendant dendritic R-functionality. It associates, via hydrogen bonding interactions between the carboxylic acid moieties, to form a cyclic hexamer. For the R-group not only the generation shown, but various generation dendrimers have been used.

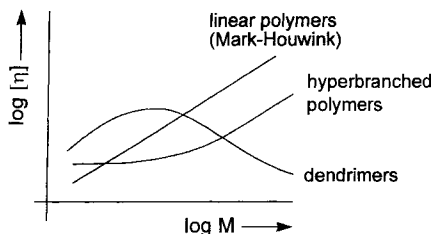
(Serroni et al., 1992; Denti et al., 1992; Campagna et al., 1995; Balzani et al., 1996). In a divergent approach, dendrimers with up to 22 metal centers have been synthesized. An example of a synthesis from one generation to the next is shown in Fig. 12-42. The use of transition metals to construct dendrimers implies that the obtained materials possess valuable optical properties (absorption of visible light, luminescence) and specific electrochemical features (oxidation and reduction levels at accessible potentials). The combination of ruthenium cations and multi-pyridine containing ligands has also been used extensively by Constable (Constable et al., 1992, 1995, 1996 a; Constable and Harveson, 1996 b; Armspach et al., 1996; Constable, 1997) and Newkome (Newkome et al., 1993 d), although these authors use the metal ions as building block connectors.

The labor intensive syntheses of totally defined, 'organic' dendrimers may inhibit bulk applications, and therefore simple one-pot procedures towards so-called hyperbranched polymers have been developed in various labs. Hyperbranched polymers share a few characteristics with their 'perfect' dendritic counterparts: Both materials are highly branched structures without crosslinks or entanglements, both are amorphous and both display low solution and melt viscosities (dendritic materials can be used as rheology modifiers). As opposed to dendrimers, the relationship between the intrinsic viscosity of hyperbranched polymers and their molecular weights does not show a maximum (see Fig. 12-43). In this respect, hyperbranched polymers resemble linear polymers.

Flory (1952) was the first to describe hyperbranched polymers by presenting a theo-



**Figure 12-42.** Balzani's approach towards metal-containing polypyridine dendrimers. In the growth step, new metal centers are introduced. In the deprotection step, vacant coordination sites are created. a) i.  $\text{AgNO}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{EtOH}$ , ii.  $\text{NH}_4\text{PF}_6$ ; b) 1,4-diazabicyclo[2.2.2]octane (DABCO),  $\text{MeCN}$ .



**Figure 12-43.** The intrinsic viscosity  $[\eta]$  of polymers related to their molecular weight. Schematic representation.

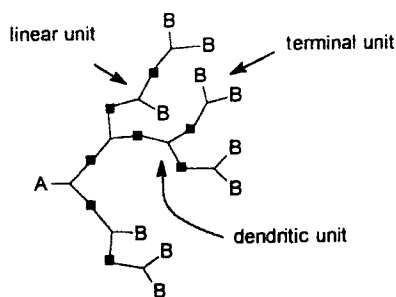
retical treatise on the polycondensation of  $\text{AB}_x$  monomers. One of the characteristics of hyperbranched polymers is the 'degree of branching' (DB), also called the 'branching efficiency' ( $\alpha$ ) or 'the branching factor' ( $f_{\text{br}}$ ). The definition of the degree of branching which is used most frequently was introduced by Fréchet (Hawker et al., 1991)

(see Fig. 12-44).

$$\text{DB} = \frac{\Sigma \text{ dendritic units} + \Sigma \text{ terminal units}}{\Sigma \text{ linear units} + \Sigma \text{ dendritic units} + \Sigma \text{ terminal units}}$$

For perfect dendrimers, for hyperbranched polymers that have been produced in a random polycondensation of  $\text{AB}_2$  monomers, and for linear polymers, the DB values are 1, 0.5, and 0, respectively<sup>10</sup>. In order to effectively compare different  $\text{AB}_x$  systems, Frey (Hölter et al., 1997) has introduced the ANB parameter, defined as the average number of nonlinear branches per nonterminal unit. The author also pointed out three ways to obtain hyperbranched polymers with DB levels higher than 0.5: (i) the use of  $\text{AB}_x$  monomers that facilitate higher reactivities for linear versus terminal units, (ii) the polymerizations of prefabricated





**Figure 12-44.** The three types of repeating units that can be found in hyperbranched polymers: linear, terminal, and dendritic (the single monomeric unit at the focal point is ignored).

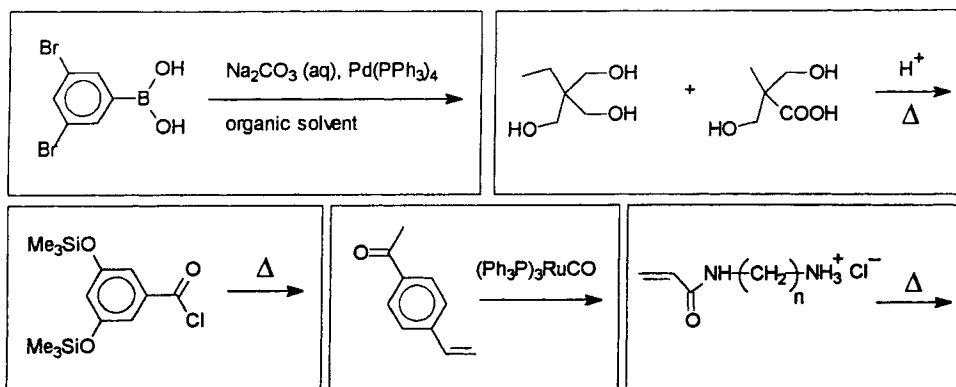
dendron monomers, and (iii) the use of slow addition/dilution techniques. The maximum DB obtainable via the latter method is 0.67. In theory, the DB and ANB parameters nicely describe the branching of dendritic materials; in practice, however, these parameters *cannot always* be determined.  $^{13}\text{C}$  NMR can sometimes be used to quantitatively differentiate between the various repeating units and can therefore be used to determine the DB (Hawker et al., 1991). Other techniques to estimate the branching factor include chain end modification of hyperbranched polymers followed by the quantitative analysis of the fully hydrolyzed materials (Kam-bouris and Hawker, 1993).

After the initial paper on hyperbranched polymers by Kricheldorf in 1982 (Kricheldorf et al., 1982), the interest in these polymers has increased, yielding, for example, hyperbranched polyesters (Hawker et al., 1991; Kricheldorf et al., 1982, 1995; Woolley et al., 1994a, b; Turner et al., 1993, 1994; Malmström et al., 1995), polypheny-

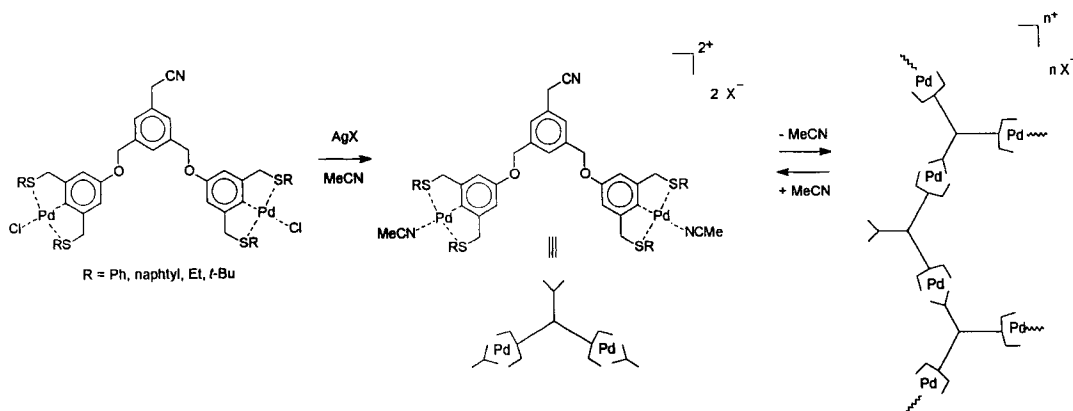
lenes (Kim and Webster, 1992a), polyethers (Uhrich et al., 1992; Miller et al., 1993), polyether (ketones) (Chu and Hawker, 1993), polyurethanes (Spindler and Fréchet, 1993; Kumar et al., 1996), polyamines (Suzuki et al., 1992), polystyrenes (Lu et al., 1996), and polycarbosiloxanes (Mathias and Carothers, 1991; Muzafarov et al., 1995). Liquid-crystalline branched polymers have also been produced (Bauer et al., 1993; Percec and Kawasumi, 1992; Percec 1994, 1995; Kim, 1992b). Usually, hyperbranched polymers are produced in one-pot syntheses using  $\text{AB}_2$  monomers. Sometimes, a small amount of a multifunctional  $\text{B}_3$  core molecule is added. In Fig. 12-45, various starting molecules are shown that have been converted to hyperbranched polymers. Feast (Hobson et al., 1997) has shown that *N*-acryloyl-1, $\omega$ -diaminoalkane hydrochloride can be polycondensed leading to the hyperbranched analogs of Tomalia's PAMAM dendrimers. The ethane derivative shows an unexpectedly high DB of  $>0.9$ , a figure derived from  $^{15}\text{N}$  NMR data. The PAMAM analogs with longer spacers show lower DBs (e.g., for the butane derivative, a DB of ca. 0.7 has been reported).

Reinhoudt (Huck et al., 1995), has applied palladium cations as connectors to build up hyperbranched materials. The synthesized building blocks consist of  $\text{Pd}(\text{II})$  square planar complexes with an inert tridentate ligand and a kinetically labile cyano ( $\text{MeCN}$ ) ligand (see Fig. 12-46). When  $\text{MeCN}$  is removed by evaporation, the building blocks form hyperbranched molecules which organize into granules with diameters ranging from ca. 100 to 400 nm. AFM data confirm the spherical shape of the aggregates. Depending on the nature of the counter anions  $\text{X}^-$  and the R-groups, the dimensions of the spheres can be adjusted. QELS (quasi elastic light scattering) data show that, in general, smaller spheres are formed

<sup>10</sup> This does not imply that a hypothetical hyperbranched polymer with a DB of 1 is a perfect dendrimer. In a perfect dendrimer, the number of covalent bonds to the focal point (or the core) is equal for all end functionalities. This is not the case for hyperbranched polymers with a DB of 1 (every branch can be of a different generation).



**Figure 12-45.** The one-pot syntheses of hyperbranched polymers from various starting materials. Clockwise from top left: (3,5-dibromophenyl)boronic acid (Kim and Webster, 1992 a), 2,2-bis(hydroxymethyl)propionic acid (monomer) in combination with 2,2-bis(hydroxymethyl)butan-1-ol (core) (Malmström et al., 1995), the HCl salt of *N*-acryloyl-1, $\omega$ -diaminoalkane (Hobson et al., 1997), 4-acetylstyrene (propagation proceeds at the 3 and 5 positions in both the Markovnikov and the anti-Markovnikov fashion) (Lu et al., 1996), and 3,5-bis(trimethylsiloxy)benzoyl chloride (Hawker et al., 1991).

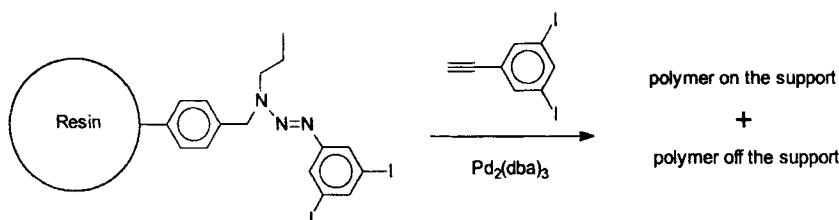


**Figure 12-46.** The construction of hyperbranched systems using AB<sub>2</sub> building blocks with suitable ligands for Pd(II) square plane complexation: one labile cyano ligand and two tridentate 'pincer' ligands.

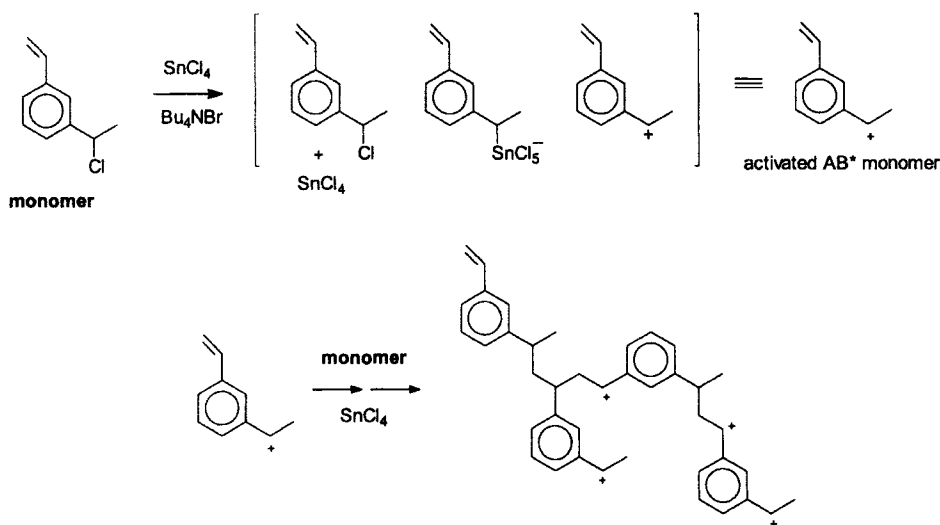
with bulkier anions or R-groups. This result can be rationalized by assuming that the growth of the granules stops when the anions can no longer compensate for the accumulating charges in the granule and start to occupy the surface. Thus, for this polymerization system, tailoring of the (nanoscopic) dimensions of the granules is possible.

Moore (Bharati and Moore, 1997) has also reported a self-regulating polymerization

system for an AB<sub>2</sub> monomer (see Fig. 12-47). The polycondensation of 3,5-diiodophenylacetylene was conducted in a piperidine solution containing the monomer, a solid support, and a palladium catalyst. Polymer formed both on and off the support. Remarkably, the polymer on the support had a much lower dispersity (as low as 1.3 versus a value >25). Moreover, the molecular weight of the polymer on the support could be regulated by adjusting the reaction conditions



**Figure 12-47.** The production of a hyperbranched phenylacetylene polymer on a solid support.

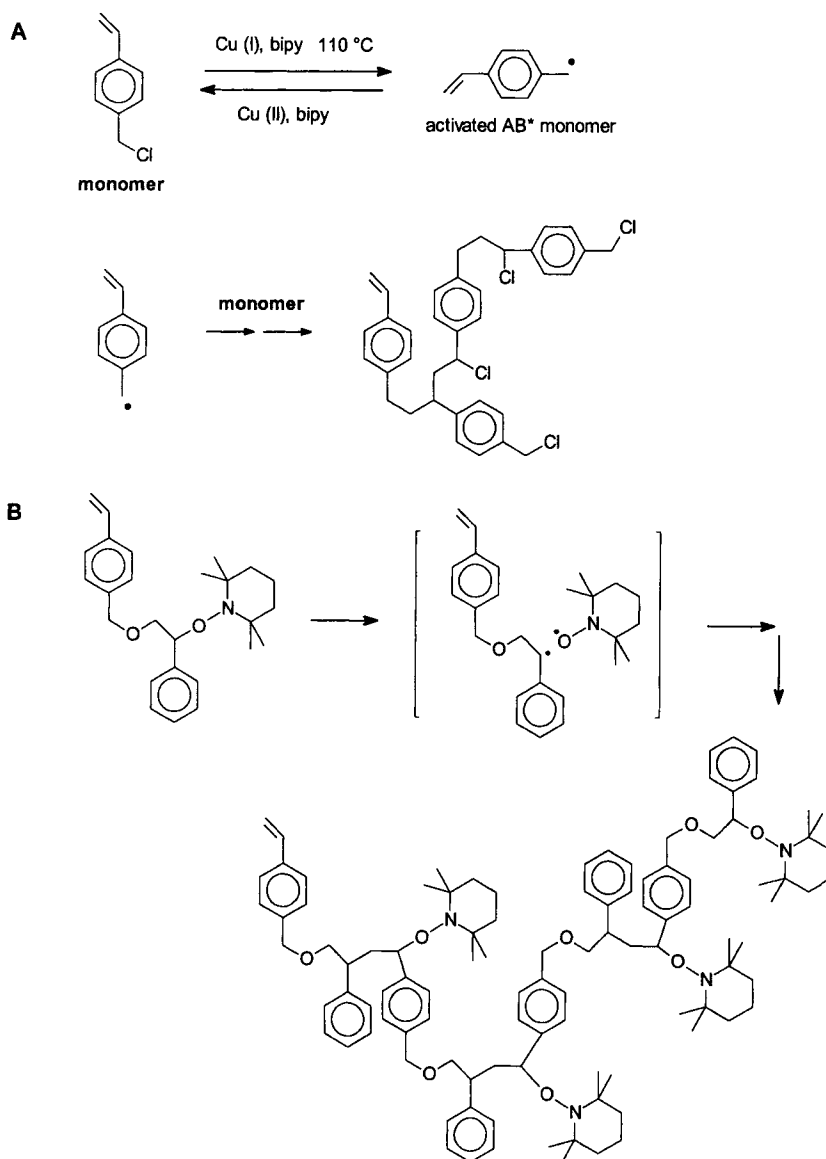


**Figure 12-48.** The self-condensing vinyl polymerization (SCVP) of a styrene derivative, as reported by Fréchet (Fréchet et al., 1995).

(e.g., the nature of the solid support and the monomer/support molar ratio at which the polymerization was conducted). Monitoring of the beads during polymerization by polarized optical microscopy showed the development of birefringence, indicating the development of stress within the beads. On the basis of this observation, an explanation for the regulated polymer growth on the bead was sought in a confinement of the propagating polymer within the boundaries of the solid support.

Relatively few of the above examples for the production of hyperbranched polymers are concerned with vinylic monomers. The

latest development in the field of dendritic materials, however, focuses on functionalized vinylic monomers of the  $\text{AB}^*$ -type. Reaction with an  $\text{AB}^*$  vinylic monomer does not only yield a propagating center, but also leads to the creation of an additional active center  $\text{B}^*$ . In this fashion, hyperbranched materials can be created. Fréchet (Fréchet et al., 1995) has reported on the so-called 'self-condensing vinyl polymerization' (SCVP) of an  $\text{AB}^*$  monomer system, i.e., 3-(1-chloroethyl)-ethenylbenzene (see Fig. 12-48). For this monomer, the active species  $\text{B}^*$  is a carbocation that is created by the addition of  $\text{SnCl}_4$ . This  $\text{SnCl}_4$



**Figure 12-49.** The synthesis of hyperbranched polystyrenes by A) atom transfer radical polymerization (ATRP) (Gaynor et al., 1996), and B) 'living' self-condensing free radical polymerization (Hawker et al., 1995). This latter method makes use of the TEMPO moiety (tetramethylpiperidine-*N*-oxide).

reagent can abstract chloro-anions at benzylic positions.

Other examples have been reported in which the active B\*-group contains a radical: Matyjaszewski (Gaynor et al., 1996) has shown that atom transfer radical polymerization (ATRP) can be used to create hy-

perbranched polystyrenes as well as polyacrylates, and Hawker (Hawker et al., 1995) has described the use of 'living' radical polymerization in the production of hyperbranched structures (see Fig. 12-49). Finally, group transfer polymerization (GTP) has also been reported as a means to yield hy-

perbranched polyacrylates (Simon et al., 1997).

## 12.4 Conclusions

The well-defined, three-dimensional architecture of dendrimers has attracted the attention of many scientists. A large number of dendritic structures has been synthesized, using one of the two synthetic methodologies available. In this chapter, we have described both methodologies – the divergent as well as the convergent methodology – by highlighting the synthesis and characterization of five different types of dendrimers. The detailed studies that have been devoted to the synthesis, molecular characterization, and specific properties of these dendrimers indicate the most important differences between the two methodologies from a synthetic point of view. The ‘polymeric nature’ of the divergent approach results in a small number of statistical defect structures in the synthesis of every generation. These defects are the result of the many reactions that have to be performed on the same molecule. Furthermore, almost no possibilities exist for the purification of intermediate generations. Illustrative of the sort of purities that can be achieved for divergently produced dendrimers is the ‘perfection’ of the fifth generation poly(propylene imine) dendrimer (see Fig. 12-1): It has a polydispersity of ca. 1.002 and a dendritic purity of ca. 20%. The ‘organic nature’ of the convergent approach results in defect-free dendrimers due to (i) the limited number of reactions performed on the same molecule on going from one generation to the next and, as a consequence of this strategy, (ii) the ease of purification of intermediate generations. However, the small differences in purity between the divergently produced structures on one hand, and the convergently synthesized

structures on the other, are not expressed in differences in the overall properties of these two classes of dendrimers. Therefore, all dendrimers, regardless of the synthetic approach, can indeed be considered as the most defined synthetic macromolecules known today. They not only have a well-defined molecular structure, but they also have a well-defined three-dimensional architecture.

After years of dedicated synthesis and characterization of dendritic macromolecules, this field of chemistry has arrived at a point at which the specific features of dendritic products and materials have to be explored more intensively. Already, dendritic molecules are used in supramolecular polymer chemistry and in the emerging field of nanotechnology. In the near future, dendrimers might be put to use in new devices. Many different applications for dendritic materials have been brought forward in the last decade and some of these are worth investigating. Fortunately, investment in this research area is facilitated by the fact that nowadays several types of thoroughly studied dendrimers are commercially available. Moreover, hyperbranched polymers (polymers closely related to their ‘perfect’ dendritic counterparts) are also easily accessible. With dendritic structures in hand, it has become possible to stretch the possibilities for these materials even further.

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## 13 Diels-Alder Ladder Polymers: Synthesis and Aromatization

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## List of Symbols and Abbreviations

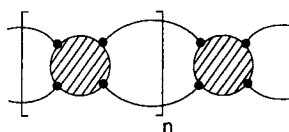
$E$	potential
$I$	current
$M_n$	number-average molecular weight
$n$	number
$P_n$	number-average degree of polymerization
$\lambda$	wavelength
CPMAS	cross-polarization/magic angle spinning
DA	Diels-Alder
DDQ	2,3-dichloro-5,6-dicyanobenzoquinone
DP	polydispersity
GPC	gel permeation chromatography
MD	molecular dynamics
NMR	nuclear magnetic resonance
PAH	polyaromatic hydrocarbon
TBA	tetrabutylammonium
TBAPF <sub>6</sub>	tetrabutylammonium hexafluorophosphate
<i>p</i> -TSOM	<i>p</i> -toluene sulfonic acid
UV	ultraviolet

## 13.1 Introduction

Ladder (ribbon) polymers consist of cyclic subunits, which are connected to each other by two links attached to different sites of the respective subunits. Thus ladder polymers have two independent strands of regularly tied bonds which do not merge into a single or double bond or cross each other as in a spiro connection (Fig. 13-1) (Overberger and Moore, 1970). In the initial phase of the history of ladder polymers, this unique structural feature was believed to make the polymers ideal candidates for applications requiring materials with high thermal, mechanical, and chemical stability. This was rationalized by the fact that the molecular weight of ladder polymers remains constant, even if one of the two strands breaks. However, it quickly turned out that, due to their poor solubility and infusibility, processing of these polymers was almost impossible. Consequently, useful materials with the expected properties could not be obtained and the first generation of ladder polymers did not gain industrial importance (Overberger and Moore, 1970; Yu et al., 1990).

Since the mid-1980s, there has been much interest in the nonlinear-optical as well as the electrical properties of rigid-rod polymer films. High optical nonlinearities derived from  $\pi$ -conjugation, high laser-damage thresholds, and the capability to form electrically conductive materials upon doping suggested conjugated ladder polymers as potentially very interesting candidates for such applications and led to a revival of interest in this class of polymers (Yu and Dalton, 1989; Dalton et al., 1989; Dalton, 1989; Belaish et al., 1989; Dahm et al., 1990).

However, progress in the synthesis of ladder polymers has not kept pace with the rapidly growing technological importance of these materials. The strategies used today still stem from the early days of ladder-poly-



**Figure 13-1.** General representation of the structure of a ladder polymer with cyclic subunits and two independent strands of bonds.

mer synthesis, some 30 years ago. Very little conceptual development has taken place towards the synthesis of well-defined and fully characterizable ladder polymers. The situation is best described by the 1990 statement by Dalton: "in fact, no one to date has ever made and unambiguously characterized a complete (classical) ladder polymer" (Yu and Dalton, 1990). Undoubtedly, the synthesis of a truly double-stranded polymer is a real synthetic challenge, considering that even the synthesis of well-defined single-stranded polymers is sometimes difficult to achieve. In the case of ladder polymers, two links have to be tied  $n$ -times between every two subunits without generating defects! This chapter intends to show that there are tools available to the chemist, which have previously been almost completely disregarded, that allow the synthesis of a whole new family of structurally perfect ladder polymers (Schlüter, 1991a; Schlüter et al., 1996). It demonstrates that they can be designed so that they may serve as precursors for their fully unsaturated counterparts. If a precursor strategy is to be reasonably applied, the precursors must be fully characterized before their transformation into the final target structures. This chapter therefore puts quite a lot of emphasis upon the description of how the precursor ladder polymers are obtained and into what depth their structures and shapes are investigated before attempts to convert them into their unsaturated, aromatic counterparts are presented.

## 13.2 Synthesis

### 13.2.1 Classical Routes – A Critical Perspective

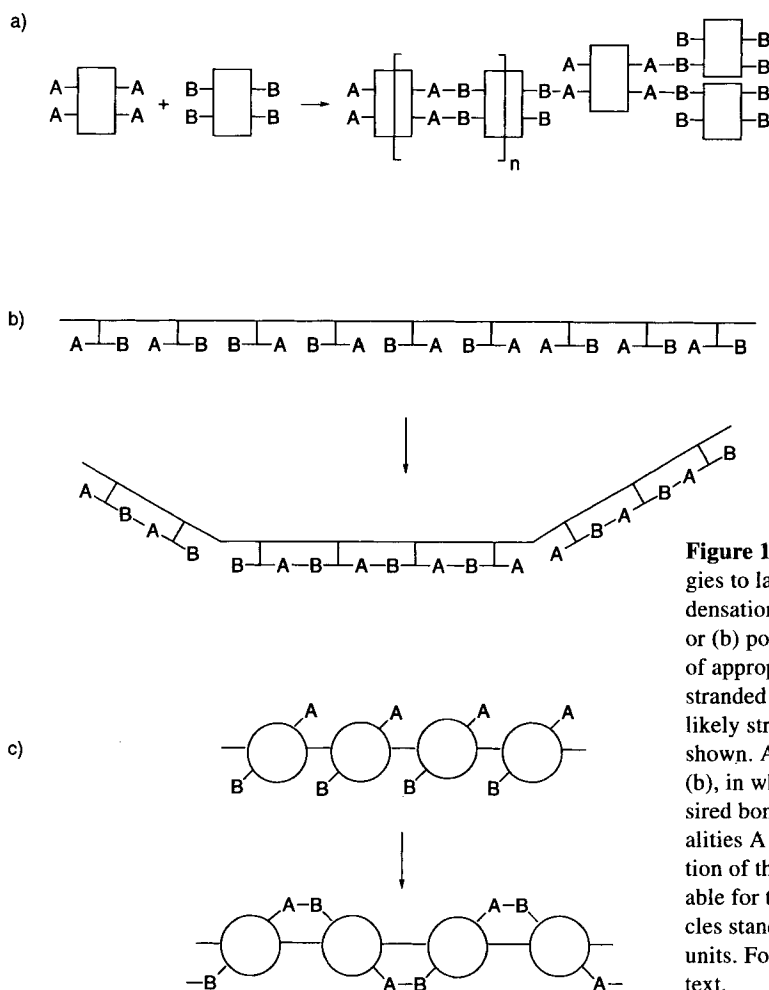
Most of the known syntheses of ladder polymers fall into two categories. In the first, two tetrafunctional monomers are made to react with each other, whereby, assuming the reaction proceeds in the desired way, the double-stranded structure grows from the very beginning (Fig. 13-2a) (Schlüter, 1991a; Bi and Litt, 1987). In the second, single-stranded polymers are synthesized which carry the required functionalities at defined, regular distances along the chain. These functionalities are then used to generate the second strand in a series of polymer analogous reactions (Fig. 13-2b) (Bi and Litt, 1987; Scherf and Müllen, 1992, 1995; Scherf, 1997). Both strategies have serious disadvantages.

In the first case, it is difficult to see which factors, under homogenous reaction conditions, would force the monomers to react exclusively in the desired way. One wrong linkage, as indicated in Fig. 13-2a, inevitably leads to inter-ribbon crosslinking, one of the reasons for the insolubility of most of the known ladder polymers. Beside this topological issue, problems also arise from the condensation reactions that are most often used and which, per se and specifically in this case, are difficult to drive to completion. As a result of the conformational rigidity of ladder polymers, the reaction mixtures become very viscous and polymerization stops at relatively low conversion. This deficiency results not only in the formation of low molecular weight ribbons, but also in ribbons with incompletely cyclized repeat units.

The second strategy (Fig. 13-2b) looks very elegant on paper, but can only be successful if a number of requirements are fulfilled. The AB-units attached to the single

stranded precursor polymer must react with one another (a) intramolecularly and (b) consecutively. If requirement (a) is not met, crosslinking between ladders would be the consequence, and if (b) is not met, loop formation through (a nonconsecutive) intramolecular coupling would be likely to occur. In recent years, some progress has been achieved with this kind of approach. In particular, the groups of Scherf, Tour, and Swager used carefully designed poly(*para*-phenylene)s (PPPs) as prepolymers (Scherf and Müllen, 1995; Scherf, 1997) which had the two functional groups (A and B) attached to the repeat unit in such a way that their sequence alternated along the backbone. Additionally, the PPP backbone is relatively rigid. Both factors reduce the conformational space available for A and B compared with the situation drawn in Fig. 13-2b. As a result of the orientation of these functional groups towards each other, the ladder polymers obtained have fewer defects than those where these precautions are not taken. Even though the experimental evidence for the degree of structure perfection still needs to be completed, it was shown that more than 90% of the bonds for the second strand can be closed in the desired way, a result that might not have been considered possible some 10 years ago. The reader is referred to pertinent reviews on this matter (Scherf and Müllen, 1995; Scherf, 1997).

Beside these strategy specific drawbacks, there is another serious problem inherently associated with ladder polymers; namely, their poor solubility. As a result of their rigid backbones, they show strong intermolecular interactions. These interactions are not only reflected in their desirable mechanical properties, for example, high tensile strength, but also in their undesirable insolubility, which makes all attempts at structure elucidation very difficult. Therefore if progress is to be made in the synthesis of



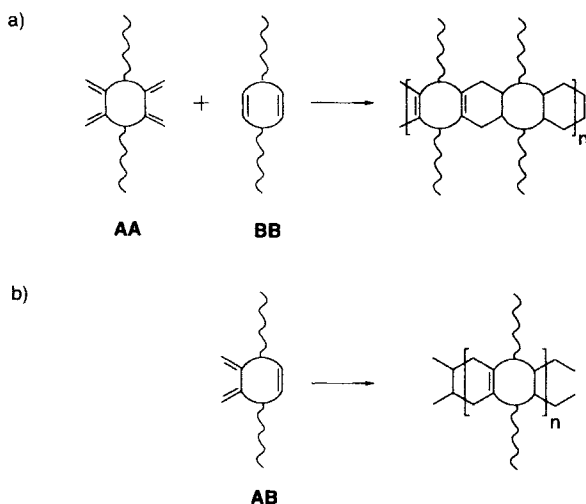
**Figure 13-2.** The two classical strategies to ladder polymers: (a) Polycondensation of tetrafunctional monomers, or (b) polymer-analogous cyclizations of appropriately substituted, single-stranded prepolymers. For both cases, likely structural irregularities are shown. An improved version of strategy (b), in which the probability of the desired bond formation between functionalities A and B is increased by a reduction of the conformational space available for them, is shown in (c). The circles stand for conformationally rigid units. For further explanation, see the text.

well-defined and characterizable ladder polymers, two main issues have to be addressed: the suppression of side reactions and the achievement of increased solubility.

### 13.2.2 Diels-Alder Route

In the course of a Diels-Alder (DA) cyclization, each of the two reaction partners pass through a transition state which is stabilized by electron delocalization, or as chemists put it, by its partially aromatic character. This stabilization is the key to perfect structures of this reaction's prod-

ucts, because it forces the reactants into the ideal relative geometry for a clean (regio-specific) reaction to take place. Thus side reactions are suppressed and yields are high (Sauer, 1967). For these reasons, the DA methodology was selected as the main tool for structure control in a new synthetic strategy to ladder polymers, a general representation of which is shown in Fig. 13-3. Bailey was one of the first to realize the usefulness of the DA reaction for the synthesis of ladder polymers, but unfortunately met with limited success due to lack of suitable monomers (Bailey and Feinberg, 1967).



**Figure 13-3.** Diels-Alder polyaddition strategy for the synthesis of structurally well-defined ladder polymers using (a) bifunctional dienes (AA-type monomers) and bifunctional dienophiles (BB-type monomers), and (b) bifunctional DA components with both diene and dienophilic functionalities (AB-type monomer). The solubility enhancing alkyl chains are indicated as wavy lines (typically hexyl).

The second issue, the insolubility problem, is accounted for in Fig. 13-3 by the attachment of flexible alkyl chains, rings, or loops. This method is known to significantly increase the solubility of rigid molecules in both polymer and low molecular weight chemistry. It should be mentioned that a strategy based on DA polyaddition necessarily yields ribbons whose molecular structure consists of a rather complex (generally statistical) sequence of *exo/endo* stereoisomers. This feature, which is associated with kinks in the backbone, may be considered as aesthetically unpleasing, but certainly helps keep the polymer in solution, and is therefore an additional plus of the strategy. Also, the DA strategy inevitably yields ladders that contain saturated ( $sp^3$ -hybridized) carbon atoms in the backbone. Depending on the respective monomers, the backbone may contain, for example, heteroatom bridges and/or (adjacent) hydrogen atoms. If the targeted polymer analogous conversion of these precursor ladders is to be brought about, these saturation sites ought to be removable by some very mild and controllable chemistry.

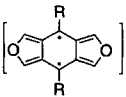
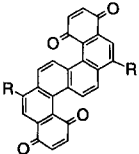
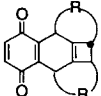
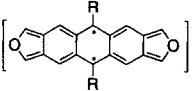
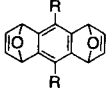
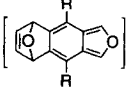
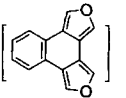
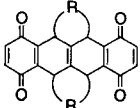
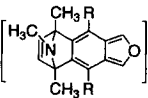
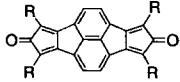

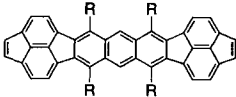

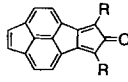

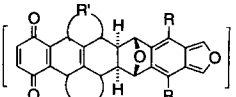
Suitable bifunctional DA monomers for the strategy outlined in Fig. 13-3 were se-

lected in strict accordance with the following criteria:

- Good accessibility on the gram or larger scale.
- Existence of structural features that help increase the solubility of the polymer.
- Irreversibility of each single DA cyclization.

The sets of synthesized monomers are shown in Table 13-1. The monomers comprise bisdienes, bisdienophiles, and diene-dienophiles, which are classified as AA-, BB-, and AB-type monomers, respectively. It goes without saying that the monomers were designed so that the equilibria of the addition reactions between them lie far on the product side. Quite a few bifunctional DA compounds are known in the literature (Christophel and Muller, 1986; Kohnke et al., 1987; Luo and Hart, 1988; Hart et al. 1983; Le Houllier and Gribble, 1983), but, unfortunately, none of them meet all the criteria, and therefore their use in polymer synthesis did not seem advisable. The DA strategy for the synthesis of double-stranded polymers has also been used by others (Scherf, 1997; Wegener and Müllen, 1993). An interesting application to hemiporphyr-

**Table 13-1.** Construction set of AA-, BB-, and AB-type Diels-Alder building blocks for the synthesis of linearly and angularly annulated ladder polymers. If not otherwise stated, R is straight alkyl, typically C<sub>6</sub> and C<sub>12</sub>.

AA	BB	AB
 <b>1</b>	 <b>5</b>	 <b>9</b> R = -(CH <sub>2</sub> ) <sub>6</sub> -
 <b>2</b>	 <b>6</b>	 <b>10</b>
 <b>3</b>	 <b>7</b> R = -(CH <sub>2</sub> ) <sub>6</sub> -	 <b>11</b>
 <b>4</b> R =  -C <sub>12</sub> H <sub>25</sub>	 <b>8</b> <b>a:</b> R = -(CH <sub>2</sub> ) <sub>12</sub> - <b>b:</b> R =  -C <sub>12</sub> H <sub>25</sub>	 <b>12</b> <b>a:</b> R = -(CH <sub>2</sub> ) <sub>12</sub> - <b>b:</b> R = -CO <sub>2</sub> C <sub>12</sub> H <sub>25</sub> <b>c:</b> R =  -C <sub>12</sub> H <sub>25</sub>
		 <b>13</b> R' = -(CH <sub>2</sub> ) <sub>6</sub> -

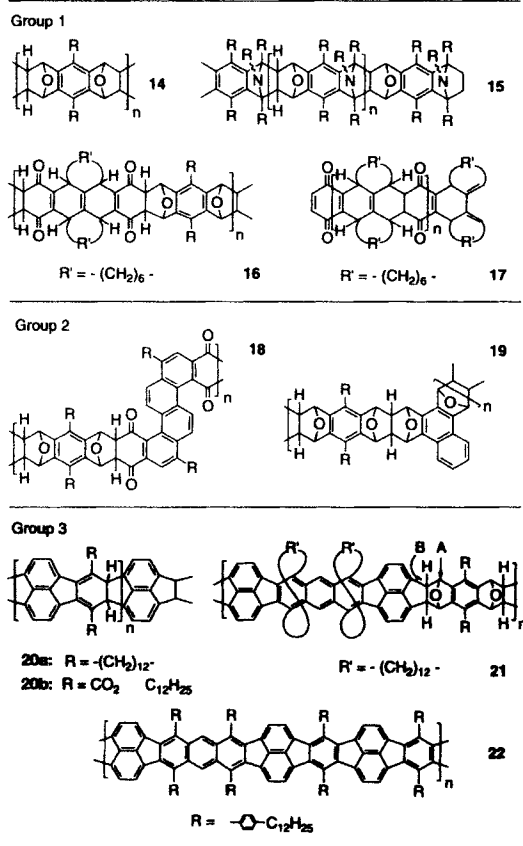
azines and phthalocyanines has recently been published (Rack and Hanack, 1994; Stihler et al., 1997).

Monomers **4** (Schulte and Schlüter, 1997), **5** (Blatter et al., 1989), **6** (Vogel et al., 1989), **7** (Schlüter, 1991 b), **8** (Löffler and Schlüter, 1994; Schlicke et al., 1996), **9** (Godt et al., 1989; Godt and Schlüter, 1991), and **12** (Schlüter et al., 1994; Schlicke et al., 1995; Schlicke, 1996) were prepared and used on the 1–10 g scale; monomers **1** (Blatter and Schlüter, 1989 a), **2** (Kintzel and Schlüter, 1997), **3** (Packe et al., 1992),

**10** (Vogel, 1990), **11** (Löffler et al., 1993), and **13** (Kintzel et al., 1998) were generated from the precursor molecules and used in situ, typically on the 5 g scale. The formulae of **1–3**, **10**, **11**, and **13** do not represent proven molecular structures, but serve as a rationalization for the observed DA reactivity of postulated intermediates which are generated in situ from stable precursors. Monomers **1**, **6**, and **12** differ from standard compounds as they are only substituted with alkyl chains or loops. Monomers **8a** and **12a** are bridged over by flexible alkyl loops



**Table 13-2.** Selected Diels-Alder ladder polymers. If not otherwise stated, R is straight alkyl, typically C<sub>6</sub> and C<sub>12</sub>.



(ansa compounds). These loops are effective solubilizers for entropic reasons (e.g., straight alkyl chains) and for enthalpic reasons because they disturb the packing of the corresponding polymers. Polymers **14–17** (Table 13-2) were obtained by combining these monomers properly like building blocks in a construction set. For example, the AA monomer **1** was reacted with exactly the same stoichiometric amount of any of the BB monomers **5–8** to give polymers **18** (Blatter and Schlüter, 1989 a), **14** (Vogel et al., 1989), **16** (Kintzel et al., 1996), and **21** (Löffler et al., 1994), respectively.

On the other hand, simple thermal treatment of the AB building blocks **9–13** or the

precursors thereof gave polymers **17** (Godt et al., 1989), **14** (Vogel et al., 1989), **15** (Löffler et al., 1993), and **20** (Schlüter et al., 1994; Schlicke et al., 1995; Schlicke, 1996), respectively (Table 13-2). The yields were almost quantitative. All the ladder polymers obtained turned out to be soluble in common organic solvents like chloroform, tetrahydrofuran, and benzene, etc., at room temperature, a result that nicely underlines the effectiveness of both the alkyl substitution and the irregular sequence of kinks in the backbone. The high solubility enabled careful structure elucidation of the polymers to be carried out.

Table 13-2 divides the polymers **14–22** into three groups according to the structural features of their backbones. This division will gain some importance in the last part of this article in the discussion of the polymer analogous transformation of these polymers into fully unsaturated ladders. Group 1 polymers **14–17** consist of a linear sequence of six-membered rings. Group 2 polymers **18** and **19** are also made up of six-membered rings, but they are annulated angularly. Finally, Group 3 polymers **20–22** are again linearly annulated, but they contain six-membered as well as five-membered rings.

## 13.3 Characterization

### 13.3.1 Molecular Structure

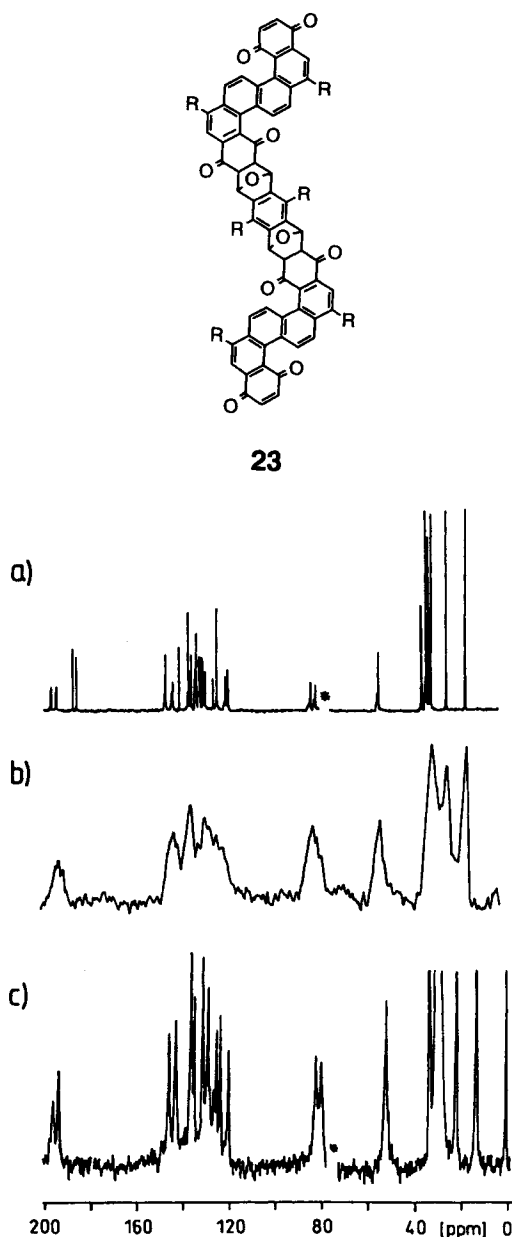
The molecular structures of the repeat units of all new ladder polymers were investigated and proven by high resolution NMR spectroscopy. In most cases, the assignment of signals rests upon detailed analyses of the NMR spectra of corresponding model compounds. Particularly informative is the structure elucidation of ribbon **18** (Table 13-2), which is described briefly here. For comparison, the 15-ring system **23** (Fig. 13-4)

was prepared as a mixture of stereoisomers (Blatter and Schlüter, 1989b). Figure 13-4 shows the high resolution NMR spectra of this model (a) and of ribbon polymer **18** (c). The match of both spectra is excellent, except for the marked signals of **23** at about  $\delta = 190$  ppm, which do not have a counterpart in the polymer spectrum. However, these signals were shown to be caused by the quinoid end groups and should therefore not appear in the polymer spectrum. The fact that this is actually observed establishes the proposed structure of **18**.

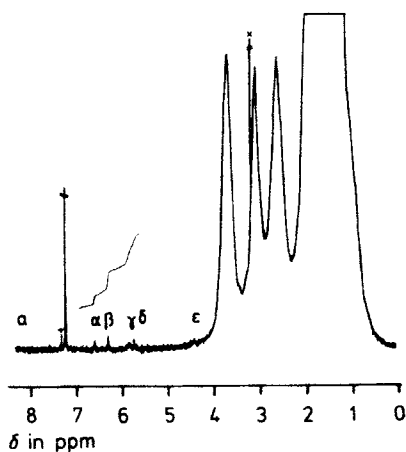
Figure 13-4 contains another interesting piece of information related to the solubility question. Polymer **18** was also prepared with the shorter hexyl chains, but the solubility of the material turned out to be too low for recording a high resolution  $^{13}\text{C}$  NMR spectrum. Thus even a relatively dense substitution with hexyl chains is not sufficient in all cases. The structure of polymer **18** ( $R=\text{hexyl}$ ) was confirmed by recording a solid-state CPMAS  $^{13}\text{C}$  NMR spectrum (Fig. 13-4b). Despite the greater line widths, the match with spectra (a) and (c) is convincing.

A second example may illustrate the great depth in which the structures of DA ladder polymers were investigated. Figure 13-5 shows the  $^1\text{H}$  NMR spectrum of **17** (Table 13-2). It goes without saying that the main signals are in full agreement with its structure. Attention was focused on the signals marked  $\alpha-\epsilon$ , which have very low intensities. What is the origin of these signals? This question requires explanation if the molecular structure of the ladder polymer is to be rigorously proven. Fortunately, it was possible to show that the signals  $\alpha-\epsilon$  are due to end groups and are therefore not caused by structural defects of any kind (Godt and Schlüter, 1992).

Stereochemical aspects of the new ribbons were also investigated. As indicated



**Figure 13-4.** High resolution  $^{13}\text{C}$  NMR spectra of (a) model compound **23** and (c) ladder polymer **18** ( $R=\text{dodecyl}$ ), plus (b) solid-state CPMAS  $^{13}\text{C}$  NMR spectrum of polymer **18** ( $R=\text{hexyl}$ ). The signals of the quinoid end group of **23** are marked (arrow). Solvent signals (chloroform) in spectra (a) and (c) are erased for clarity (\*).



**Figure 13-5.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ) of polymer **17**. The signals due to end groups are marked with  $\alpha$ – $\epsilon$  (+: benzene,  $\times$ : *tert*-butyl methyl ether).

above, the backbones of all the ladder polymers synthesized using DA polyaddition contain complex sequences of repeating units with different stereochemistry. In the case of the angular annulated ladders, the situation is even more complex. New monomers may react with the growing chain in a cisoid or transoid fashion to the terminal repeat unit. The  $^{13}\text{C}$  NMR shifts of the atoms of a repeat unit generally depend on its stereochemistry and differ by a few parts per million. The shifts may also depend on the stereochemistry of the two neighboring repeat units. As a result, the spectra are quite complex and a reliable correlation of their stereogeometries or sequences with certain signals is difficult (if not impossible) to achieve. In order to obtain at least some quantitative data on how many and which stereoisomers are present in the backbone, and in order to get as much information about the microstructure of the polymers as possible, the following procedure was pursued for polymer **17**:

a) Pieces of the polymer backbone containing the relevant stereoisomeric forms were synthesized.

b) Single crystals of these pieces were grown and their stereochemistry was proven by X-ray diffraction.

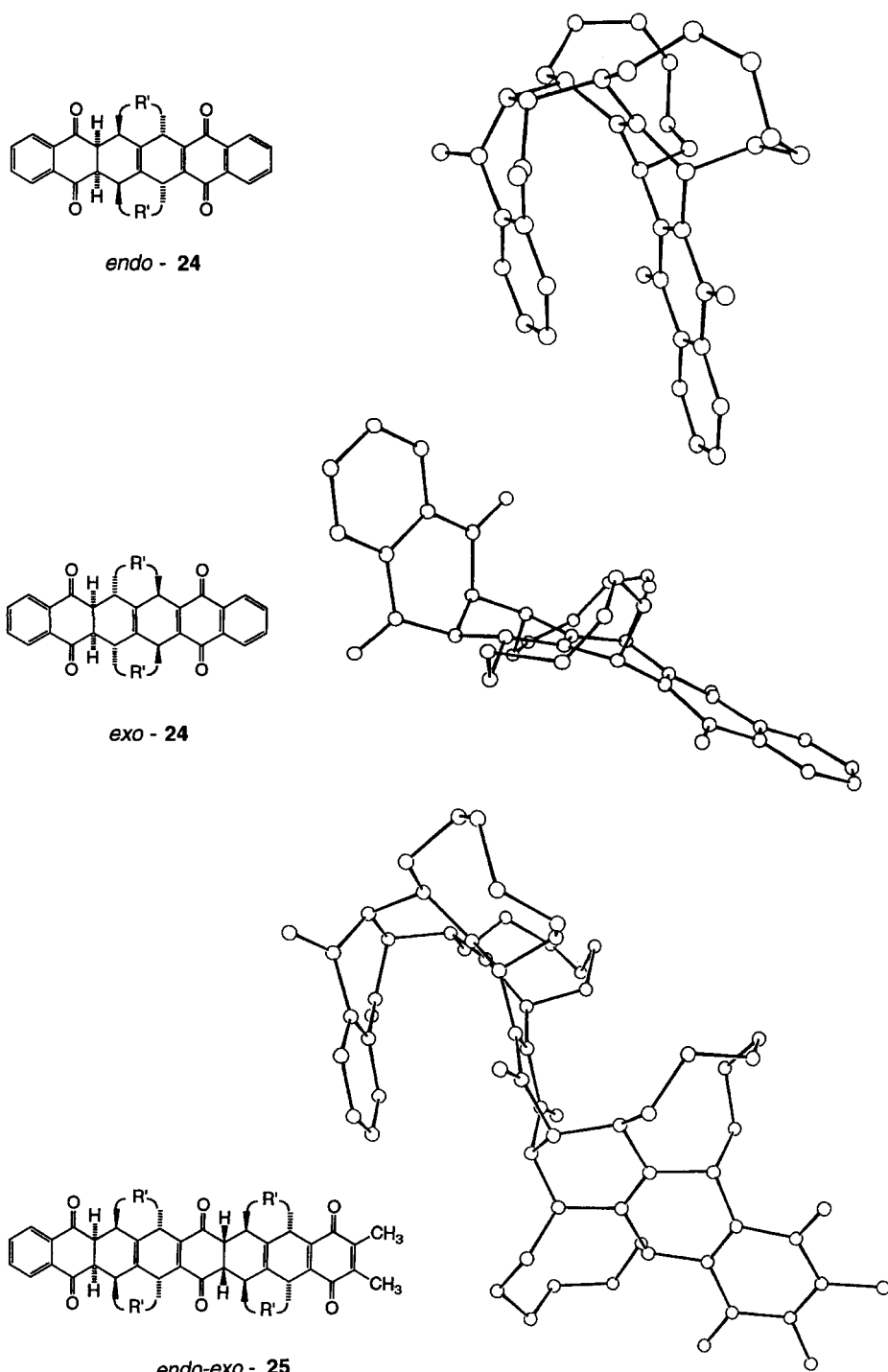
c) The NMR spectra of the dissolved single crystals was recorded.

Observed shifts were correlated with those in the polymer spectrum and the desired data was extracted. This procedure not only has the function of answering the stereochemical questions, but the results can be thought of as a starting point for future attempts to achieve the ultimate goal of a controlled stereospecific DA polymerization.

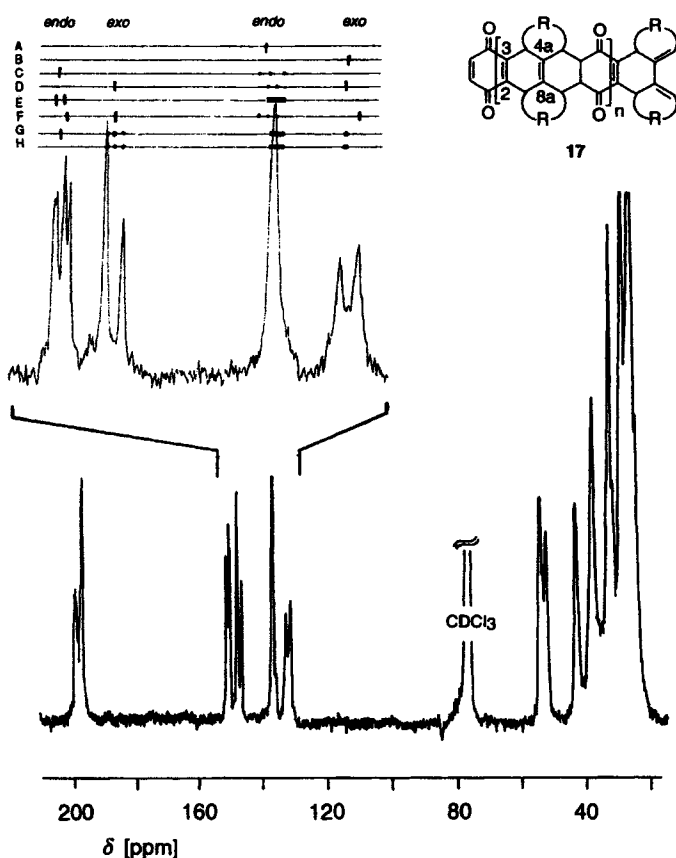
Polymer **17** contains repeat units in two stereoisomeric forms, *endo* and *exo*. Among others, the model compounds *endo*-**24**, *exo*-**24**, and **25** (Chart 13-1) (containing both *exo* and *endo* repeat units) were prepared and their structures determined using X-ray diffraction (Godt et al., 1992). Based on the analysis of the NMR spectra of these compounds, it was possible to assign groups of signals in the  $^{13}\text{C}$  NMR spectrum of **17** (Fig. 13-6) to determine whether they are associated with *exo* or *endo* repeat units. Quantitative analysis of the intensities of relevant signals yielded an *exo*:*endo* ratio of approximately 1:1. Furthermore, other information was obtained on the sequence. For example, the signal at  $\delta = 132$  ppm was assigned to all carbons C-4a(8a) in *exo* repeating units centered in *endo*-*exo*-*endo* or *endo*-*exo*-*exo* triads (Godt et al., 1992).

### 13.3.2 Shape: Three-Dimensional Versus Two-Dimensional Coils

After having elucidated the molecular structures and some aspects of their stereochemical nature, the next logical step was to investigate the secondary structure of the new ribbons. This step is a complex matter for which no experimental answers are



**Chart 13-1.** Molecular structures of model compounds *endo*-24, *exo*-24, and *endo-exo*-25.

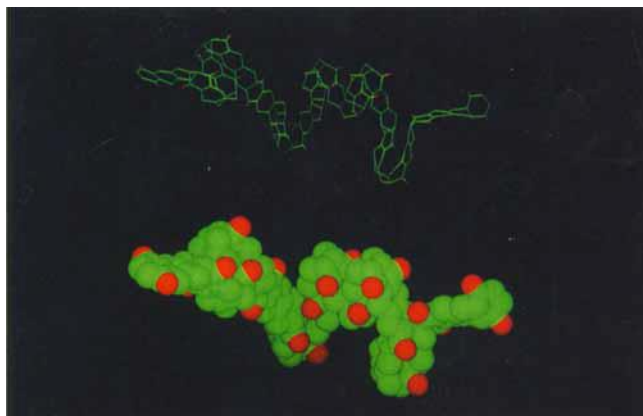


**Figure 13-6.** Fully reproducible high resolution  $^{13}\text{C}$  NMR spectrum of polymer **17**. The signals of C-2(3) and C-4 a(8 a) are grouped around  $\delta = 135$  and  $\delta = 150$  ppm, respectively. The assignment is based on eight different model compounds (A–H), as indicated in the inserted enlargement of the olefinic region of the spectrum. The structures of A–H are not shown. The signal at  $\delta = 132$  ppm is marked (\*).

available to date. However, to gain insight into the secondary structures, the X-ray data of the models for polymer **17** were used as a data set for a computer program which allows the assembly of molecule fragments to form larger ones (Schürmann et al., 1993). All available stereochemical information was considered in this process. By this means a computer model of polymer **17** was generated, whose three-dimensional views should give a realistic picture of its overall shape (Fig. 13-7). According to this picture, polymer **17** has a coiled structure, similar to the single-stranded polymers. From an inspection of the two possible stereoisomeric repeat units (see structures of *exo*- and *endo*-**24** in Chart 13-1), it is evident that the *endo*-unit is not responsible for the three-di-

mensionally coiled backbone. This unit has a mirror plane which is symmetrical to the one in which chain propagation occurs. The *exo*-unit, however, has a kink in its structure which undergoes a flipping process near room temperature. This was proven by dynamic NMR studies using *exo*-**24** as a model and reflects some torsional flexibility of the polymer backbone at each *exo* repeat unit (Godt et al., 1992).

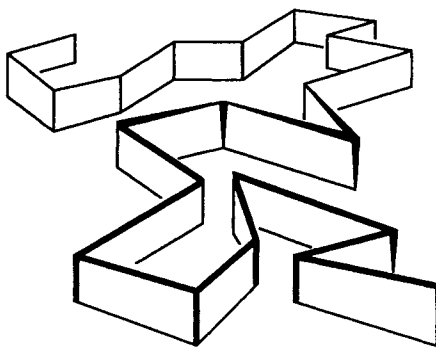
While polymer **17** and also presumably polymer **16** behave more or less like normal polymers in that they take on randomly coiled shapes, this might not be the case for polymers **14**, **15**, **20**, and **21**. These structures do not contain a cyclohexene ring, but only a linear sequence of conformationally rigid fragments (like 7-oxa(aza)norbor-



**Figure 13-7.** Computer-generated three-dimensional model of polymer **17** without hydrogen atoms and flexible alkyl rings (top), and the corresponding van der Waals plot (bottom). Carbon is in green, oxygen red.

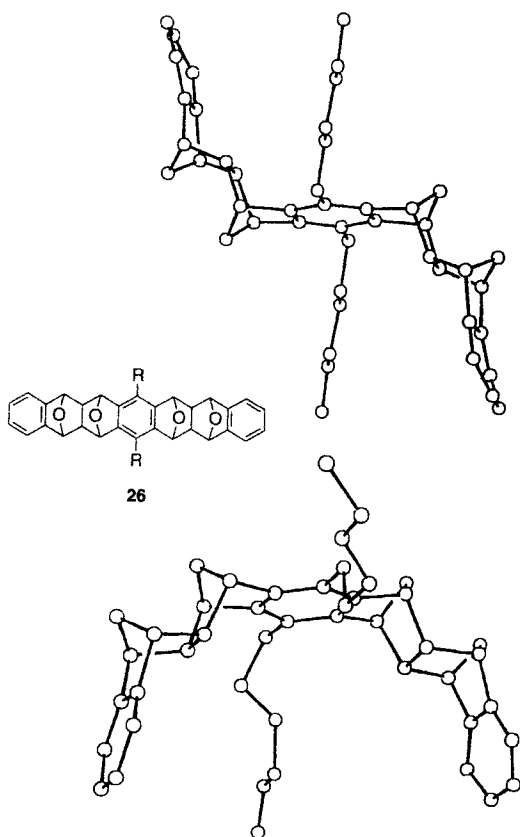
nes, benzenes, naphthalenes, and flat five-membered rings), and they have the proper symmetry elements for the polymer to show plane symmetry. If this picture holds, these polymers should have the unique shape of a two-dimensional coil or a disc (Fig. 13-8). Finally, polymer **22** should have a flat, board-like structure, which can undergo undulation and helical twist-type motions.

Compound **26**, a model for **14**, was selected to demonstrate this point. The X-ray structures of two diastereomers of **26** (Chart 13-2) show that both isomers have a mirror plane in which all the oxygen atoms lie. However, these structures and the vague description of the fragments of **14** as being rigid, are not sufficient to lead to the conclusion that structure **14** attains the shape of a (snake-like) two-dimensional coil. This would depend upon the degree of anisotropy of the flexibility of **14** in and out of the plane. We applied all-atom molecular dynamics (MD) to help solve the problem of polymer's **14** shape in solution (Schürmann et al., 1993). Oligomer **27**, which consists of seven repeat units of fragments of **14** carrying no alkyl chains and terminated by benzene rings, was selected as a model. The MD studies were carried out (a) with two differ-



**Figure 13-8.** Schematic representation of the expected secondary structure of polymers **14**, **15**, **20**, and **21**, which is a two-dimensional coil.

ent starting conformations of **27** (A and B, see Fig. 13-9) to avoid a dependence of the results upon the initial structure and (b) in the presence of solvent molecules (benzene), since polymer/solvent effects have considerable influence on the conformation of a polymer chain. The starting conformation A of model **27** was constructed by using the bond lengths and angles from the X-ray structures of **26** and the AMBER data bank, which gives it plane symmetry. Conformation B is an equilibrated structure (after 30 ps) which was created from A by performing a MD calculation in vacuo. During the calculation (without solvent), the initial-



**Chart 13-2.** Structures in the crystal of two diastereomers of model compound **26** (ORTEP).

ly two-dimensional coil starts to deviate significantly from planarity, which is initiated by higher fluctuations of the termini.

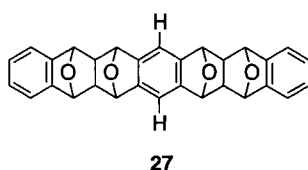
Both starting structures were placed in a box of constant volume filled with benzene molecules of realistic density at 300 K, and the molecular dynamics were simulated under periodic boundary conditions. Conformation A keeps its two-dimensional shape over the entire period of simulation (130 ps). Visualization of the molecular dynamics in a video showed that the structure retains the symmetry plane  $\sigma_{xy}$ . For starting structure B, the simulation in benzene at 300 K did not lead to any significant change of the gross conformation, even with an extended simulation time (200 ps). Therefore

the system was heated to 700 K at 100 K intervals. After each run had equilibrated, the system was cooled to 300 K. Finally, in the 700 K case for this conformation, a change in the plane-symmetrical geometry takes place. As in the case of conformation A, visualization of the molecular motion revealed that conformation B was no longer spherical, but two-dimensional and disc-like.

Thus, regardless of the starting conformation, structure **27** in benzene solution equilibrates to a two-dimensional conformation, which indicates a unique structural feature of **14** and other ladder polymers of comparable rigidity and symmetry. It is important, however, to realize that this calculation does not account for other effects that might play a role during synthesis of the polymer. It may well be the case that, as the polymer chain grows, larger fragments of the same polymer chain irreversibly overlap each other, or that intermolecular effects (for example, the formation of entanglements) prevent the polymer from relaxing into a two-dimensional geometry. Small-angle X-ray scattering is an appropriate method with which this problem can be approached experimentally.

### 13.3.3 Molecular Weights

The new generation of ladder polymers are soluble in common solvents at reasonable concentrations. This is an enormous advantage in that all typical polymer-analytical techniques can be applied. Thus it is reasonable to assume that the molecular weight data obtained are more accurate than those for classical ladder polymers. However, sufficient solubility alone does not solve all the problems. For instance, gel permeation chromatography (GPC) is of limited value because appropriate standards for ladder polymers with little flexibility are presently not available. Nevertheless, GPC mea-



**Figure 13-9.** Two different starting conformations A and B of **27**. Top and side view of A (red) and B (green).

surements were carried out but not interpreted quantitatively. In most cases, relatively broad and monomodal molecular weight distributions were obtained, indicating clean polymerizations. In the case of monomers **9** and **13**, the elution curves showed the formation of some low molecular weight material, which could easily be removed. These side products were identified as double-stranded cycles a [6]beltene derivative for **9** and an [18]cyclacene derivative for **13** (Packe et al., 1992). Table 13-3 contains a selection of representative GPC data.

The molecular weights of the ribbon polymers were determined using vapor and membrane osmometry. In order to rule out possible aggregation phenomena, only dilute solutions were measured and each molecular weight was reproduced over a range of different concentrations. According to these measurements, representative samples have about 50 repeat units on average corresponding to molecular weights of

**Table 13-3.** Selected molecular weight data of Diels-Alder ladder polymers obtained from unfractionated material using gel permeation chromatography (versus a polystyrene standard). The polydispersities (DP) are typically between 2.0 and 3.0. For the polymer structures, see Table 13-2. ( $M_n$  is the number-average molecular weight;  $P_n$  is the number-average degree of polymerization.)

Polymer	$M_n$	$P_n$
<b>14</b>	14 000–19 400	40–55
<b>15</b>	35 000–51 500	90–131
<b>17</b>	12 700–15 900	36–45
<b>20a</b>	3 500–7 900	10–25
<b>20b</b>	32 000–38 000	51–60
<b>21</b>	12 000–27 000	10–25

roughly  $M_n = 20\,000$  g/mol. Samples with higher molecular weights were easily obtained through fractionating techniques. Thus, for polymer **17**, gram fractions of material (still soluble) were prepared, which had an average molecular weight of the or-



der of  $M_n = 100\,000$  g/mol. This translates into a ribbon of 1000 linearly annulated six-membered rings, which clearly demonstrates the power of the Diels-Alder polyaddition for the synthesis of double-stranded polymers. In accordance with their relatively high molecular weight, DA ladder polymers can be cast into flexible films from solution. Group 3 polymers, except for **20b**, have lower molecular weights, as already indicated by the GPC data (Table 13-3). We believe that this is not an inherent phenomenon, but that it rather reflects the polymerization procedures of these only recently developed monomers, which have not yet been optimized.

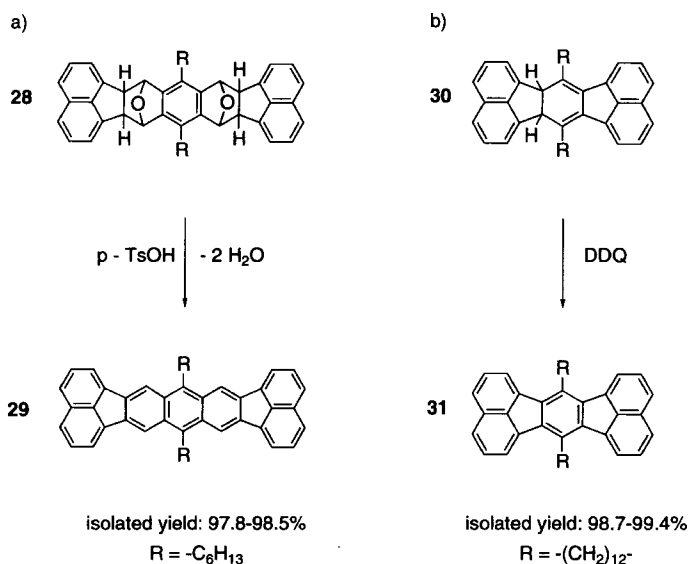
During thermal treatment, conventional ladder polymers undergo nonconcerted bond cleavage processes at sites randomly distributed over the two strands of bonds. The molecular weights remain constant until two opposing bonds are coincidentally cleaved. Since DA cyclization/recyclization is an equilibrium process, the above-described new generation of ladder polymers may exhibit an additional mode of decomposition, the retro-DA cleavage. By this reaction, two bonds of the same six-membered ring are cleaved in a concerted manner. Such a process would have a detrimental effect on the properties of DA ladder polymers in that each single retro-DA step breaks the backbone into two independent fragments, and thus decreases the molecular weight. This issue was therefore investigated in some depth using polymer **14** as a representative. Fortunately, it could be shown that no retro-reaction occurred within a reasonable temperature range (Löffler et al., 1992). Thermal treatment of **14** with a monofunctional DA component in large excess led neither to a decrease of the molecular weight nor to a broadening of the distribution. An exception here is monomer **13** for which an equilibrium between its linear oligomer and

a [18]cyclacene derivative was observed (Kintzel et al., 1998).

## 13.4 Aromatization

After the above-described aspects of DA ladder polymers had been investigated, the direction of research focused more on the ultimate goal, which is to generate fully unsaturated (aromatic), double-stranded polymers from DA ladders. The critical question which really needed to be answered was: Are DA ladder polymers appropriate precursors? The initial attempts into this matter all used Group 1 polymers, because substituted polyacenes, which would be the products, are clearly challenging targets (Kivelson and Chapman, 1983). A discussion of some of their expected properties is available in the literature (Schlüter, 1991a; Schlüter et al., 1996). Though some progress was achieved along these lines, it has to be said that synthetic chemistry has failed up to now to provide reproducible access to any polyacene derivative. This is not to say that a goal like this is intrinsically impossible to achieve. Its achievement, however, requires the development of an entirely new strategy, one which ought to avoid the wet-chemical procedures that have been tried so far. With these more or less negative results regarding Group 1 polymers in mind, Group 2 precursors were not seriously tried.

The tables turned when the investigation was extended to Group 3 polymers **20–21**. Some initial orienting model aromatizations were very successful with conversions of virtually 100%. This was an excellent basis for trying these reactions not only on models, but also on polymeric material. For example, compound **28** (Fig. 13-10, a model for polymer **21**) could be dehydrated, regardless of its actual stereochemistry, with

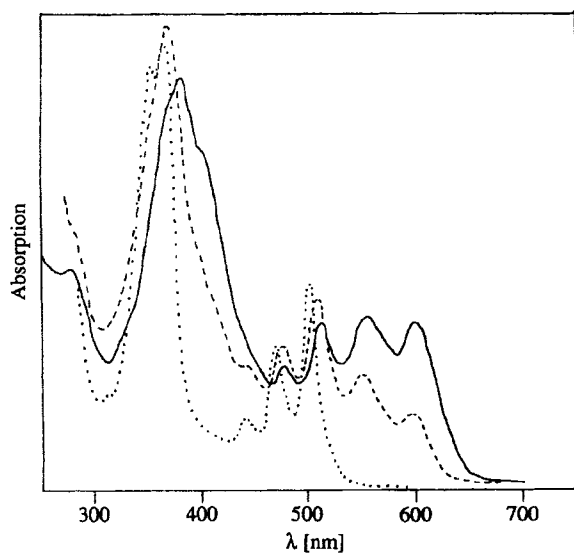
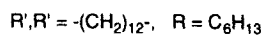
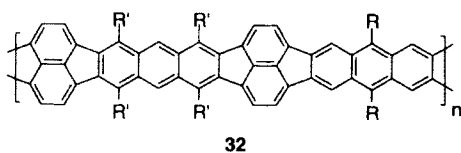


**Figure 13-10.** Model compounds **28** and **30**, and a) the dehydration of **28** to **29** and b) the dehydrogenation of **30** to **31**.

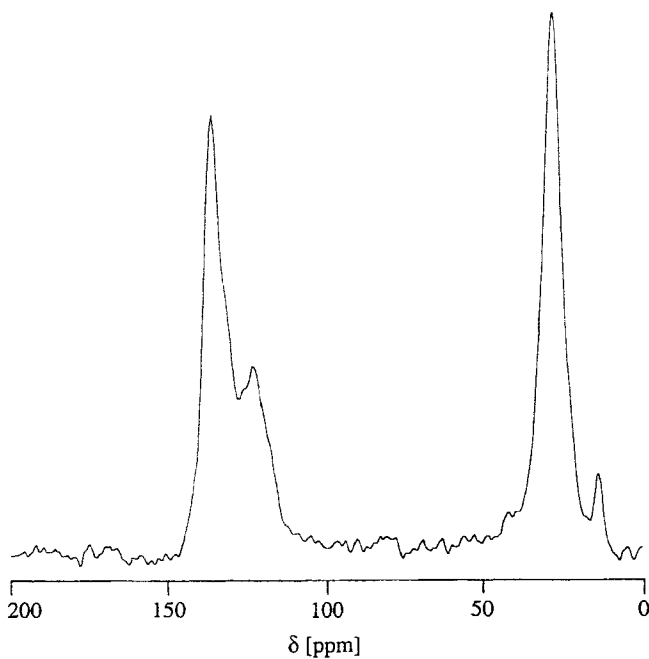
*p*-toluene sulfonic acid (*p*-TsOH) to benzo-difluoranthene **29**, which was obtained in isolated yields of 97.8–98.5% (Schirmer et al., 1993). To our knowledge, this attempt is the only one of numerous attempts where the dehydration of precursor molecules into polycyclic aromatic compounds proceeds reproducibly and absolutely cleanly. This dehydration does not lead to any kind of side reaction, which is of crucial importance for the targeted polymer analogous application. Another characteristic of this dehydration is that it does not seem to proceed catalytically. An important consequence is that the number of water molecules removed and thus the degree of both planarization and solubility can be controlled by stoichiometry. Comparably excellent results were obtained when the dehydrogenation of compound **30** was tried. This compound resembles the repeat unit of polymer **20**. Reaction of **30** with one equivalent of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), which is a powerful dehydrogenation agent, led to complete removal of the “hydrogen” (Kintzel et al., 1998). The isolated yield of **31** ranged between 98.7 and 99.4%.

These experiments laid the foundations for developing the dehydrogenation and dehydration chemistry of polymers **20** and **21**, respectively, which will be briefly described in the following.

Dehydration was achieved in full analogy to the model reaction by refluxing a solution of polymer **21** with a slight excess of *p*-TsOH per repeat unit. After a few hours, the color of the initially bright yellow solution had turned red, but stayed homogenous. Normal work-up yielded a material whose UV spectrum shows a considerable bathochromic shift in comparison with the starting material (Fig. 13-11) (Löffler et al., 1994b). Additionally, the intensities of the NMR signals of carbons A and B (structure **21** in Table 13-2) are greatly reduced to the advantage of the aromatic carbons. If the same experiment was carried out with an excess of *p*-TsOH, the dehydration could even be driven to completion. Polymer **32** was recovered as an insoluble material. Its CPMAS  $^{13}\text{C}$  NMR spectrum is depicted in Fig. 13-12. The UV spectrum, for which sparingly soluble, low molecular weight material was used, shows a significant in-



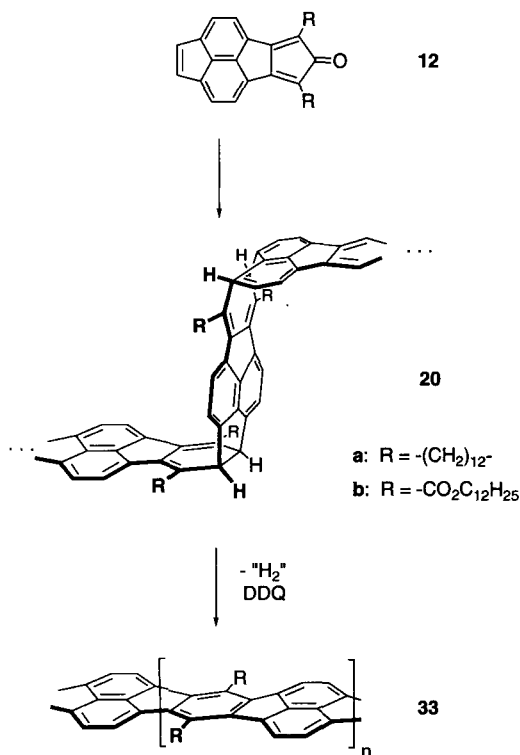
**Figure 13-11.** UV spectra (chloroform) of precursor polymer **21** (...), the 80–90% dehydrated polymer **21** (- - -), and the fully dehydrated, unsaturated polymer **32** (—).



**Figure 13-12.** CPMAS  $^{13}C$  NMR spectrum of the fully dehydrated unsaturated polymer **32**.

crease in the intensity of the long wavelength absorptions, but no further bathochromic shift of  $\lambda_{\text{max}}$ . The NMR spectrum gives no indication of "residual water" in the structure: The oxygen- and hydrogen-carrying carbon atoms of **21** (A and B) typically absorb in the ranges of  $\delta=75-85$  ppm and  $\delta=50-60$  ppm.

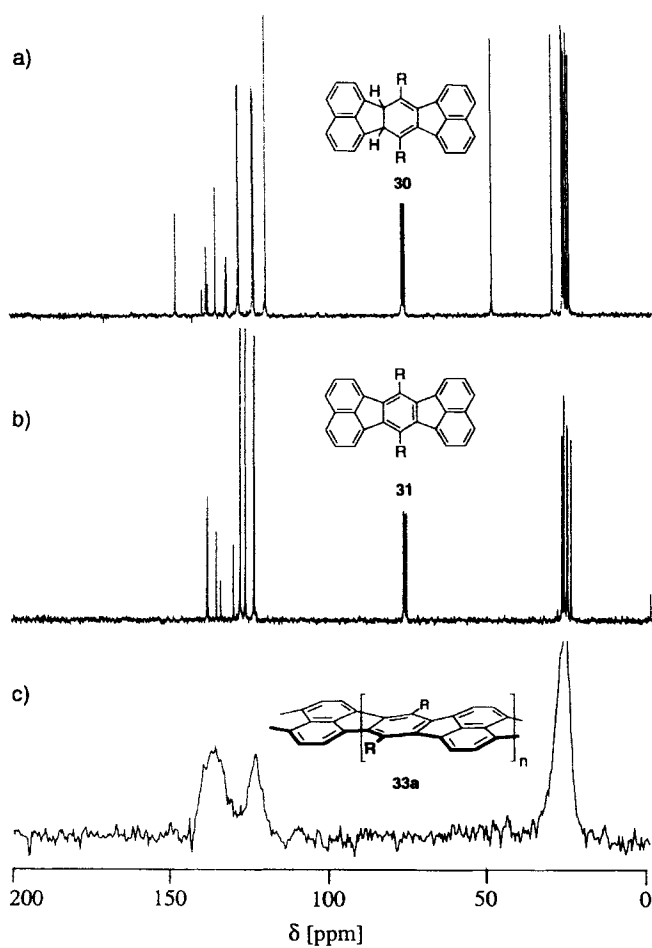
Success was also accomplished using polymer **20a** and **20b** (Fig. 13-13). The idea was to try to simply "titrate" them with DDQ. Depending on the amount of DDQ used, the degree of aromatization ought to be controllable and adjustable to the respective requirements. Ultimately, stoichiometric amounts should furnish the fully unsaturated polymers **33a** and **33b**. Experiments



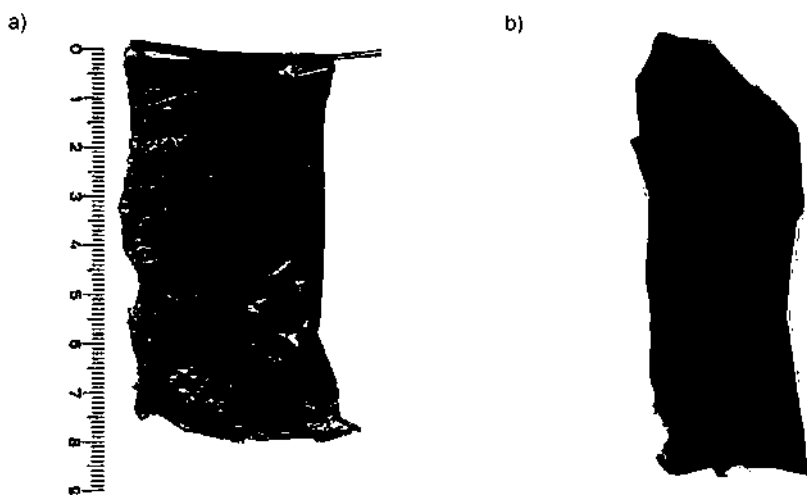
**Figure 13-13.** Polymerization of the AB-type Diels-Alder monomer **12** and dehydrogenation of the resultant precursor polymer **20** to give the fully unsaturated ladder polymer **33**.

show that this can actually be brought about. Figure 13-14 depicts the <sup>13</sup>C NMR spectra of two model compounds, **30** and **31**, and a CP MAS <sup>13</sup>C NMR spectrum of the fully unsaturated polymer **33a**. The signal of **30** at approximately  $\delta=50$  ppm does not appear in the spectrum of polymer **33a**. The UV evidence is also convincing (spectrum not shown). In the case of precursor polymer **20b**, these experiments could even be conducted on a more advanced level. Here the aromatization was not only done in a conventional flask-type set-up, but, because of the significantly higher molecular weight, also by using the precursor in film form and doing it directly on the film. Figure 13-15 compares a film of untreated **20b** with one that had been dipped into a solution of DDQ for some hours. As indicated by the red color (and some other evidence, of course), the dehydrogenation took place at the surface of the film. This is an important fact, because the considerable morphological constraints associated with this chemical process (planarization) are less detrimental to the overall mechanical stability of the final film as long as some flexible material is still available in the interior. Without this stabilization, the chemical modification would most likely result in a material that is too brittle to be used for most measurements or applications.

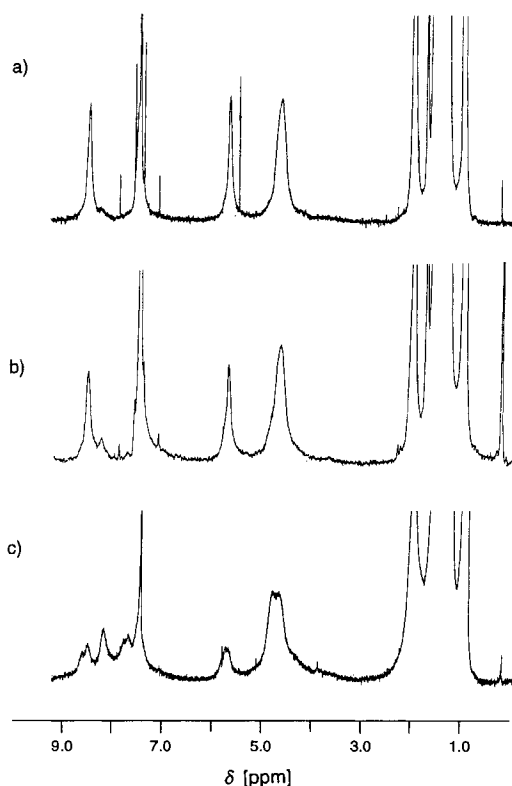
Besides these experiments with films of polymer **20b**, this precursor was also used to see whether the level of dehydrogenation can be adjusted to a certain, predetermined level. The addition of 10, 20, and 50% of DDQ per repeat unit gave polymer **20b** with approximately the same percentage of dehydrogenated repeat units, as evidenced by the respective <sup>1</sup>H NMR spectra (Fig. 13-16) (Schlicke et al., 1995). This step-wise conversion of **20b** to its unsaturated analog **33b** can be driven further. It should be noted here that after the removal of 70–80% of all the



**Figure 13-14.**  $^{13}\text{C}$  NMR spectra of the model compounds a) **30** and b) **31**, and c) the CPMAS  $^{13}\text{C}$  NMR spectrum of the fully unsaturated polymer **33a**. The signal in spectrum (a) at approximately  $\delta = 50$  ppm does not appear in spectra (b) and (c).



**Figure 13-15.** Films of precursor polymer **20b** a) before and b) after dipping into a solution of DDQ.



**Figure 13-16.**  $^1\text{H}$  NMR spectra of samples of polymer **20b** which had been treated with a) 10%, b) 20%, and c) 50% equivalents of DDQ per repeat unit. The signal at approximately  $\delta=5.7$  ppm, which corresponds to backbone saturated sites, decreases to the advantage of new signals in the aromatic region. The signal of the  $\alpha\text{-CH}_2$  groups of the ester at  $\delta=4.8$  is shifted slightly downfield at the aromatized units ( $\delta=4.7$ ).

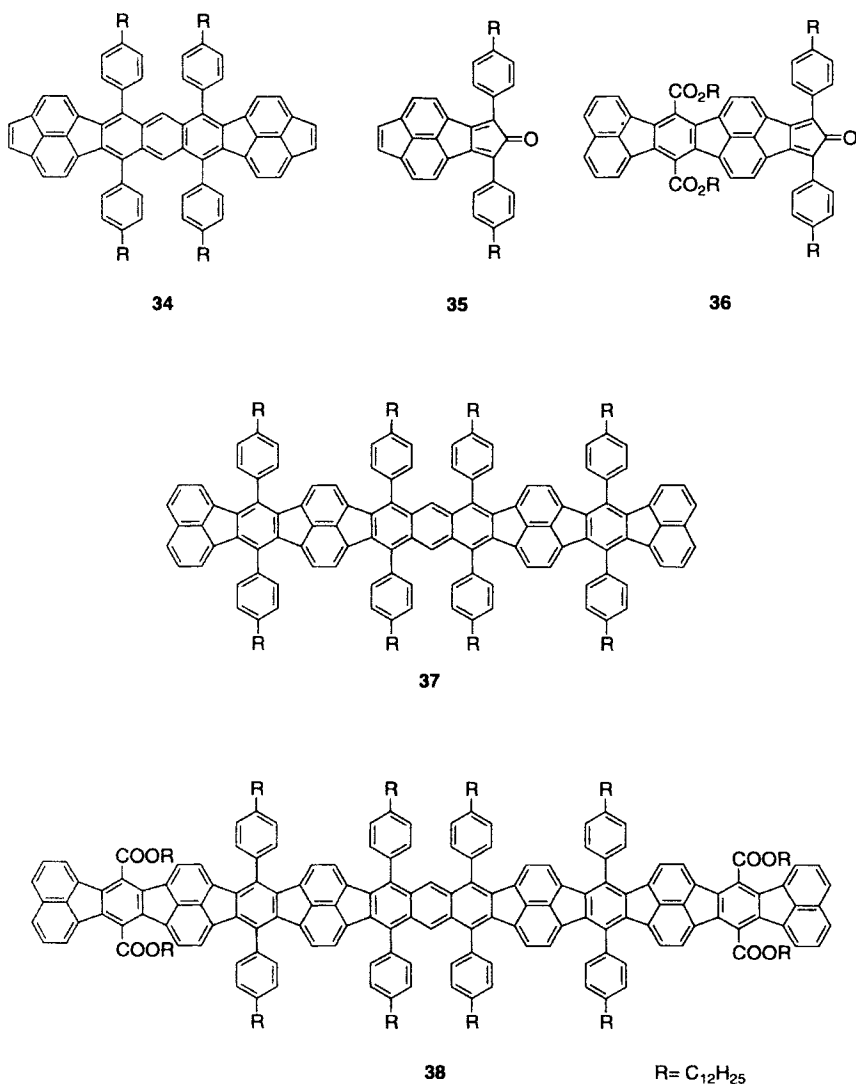
saturated positions, the solubility of the material becomes so poor that the recording of sufficiently resolved NMR spectra is practically impossible. Through the application of excess DDQ and higher temperatures, dehydrogenation can be completed.

### 13.5 Monodisperse Ladders in the Nanometer Range

With the DA technology for the synthesis of structurally defined ladder polymers

at hand, it was tempting to ask whether it can be used not only for the synthesis of polydisperse but also for monodisperse compounds. On the one hand, these compounds would serve as models for the respective polymers and, on the other, they could be used to push the size of extended polyaromatic hydrocarbons (PAHs) to its present limits. In this regard, the synthesis of PAH **37** and **38** has briefly been described (Schlicke et al., 1997). They are obtained through the end-capping of DA bisdienophile **34** with two equivalents of either the short cyclopentadienone **35** or the long one **36** (Chart 13-3). In both cases the DA reaction directly gives the fully unsaturated product, because carbon monoxide is cheletropically cleaved off in situ. The same principle was used for the synthesis of Group 3 polymer **22** from monomers **4** and **8b**. As a result of the substitution with dodecyl chains, these quite extended, flat (board-like) molecules show exceptionally high solubility in common organic solvents at room temperature. For example, dichloromethane dissolves  $5.0\text{ g l}^{-1}$  of **37** and  $4.5\text{ g l}^{-1}$  of **38** at this temperature. This enables a complete characterization. Because of their extended  $\pi$ -system, compounds **37** and **38** were studied by cyclic voltammetry (Table 13-4). Experiments were carried out in tetrahydrofuran (reductions) and dichloromethane (oxidations) under superdry conditions. Compound **37** can be reduced to the heptaanion and **38** to the octaanion within a relatively small potential range (Fig. 13-17). Fullerenes cannot be reduced further than the hexaanions. Persistent tri- and tetracations can be generated for **37** and **38**, respectively.

The PAHs **37** and **38** are 3.0 and 4.5 nm long, making **38** the most extended, fully characterized aromatic compound known today. As a result of their substitution pattern, both compounds can be handled like low molecular weight ones.

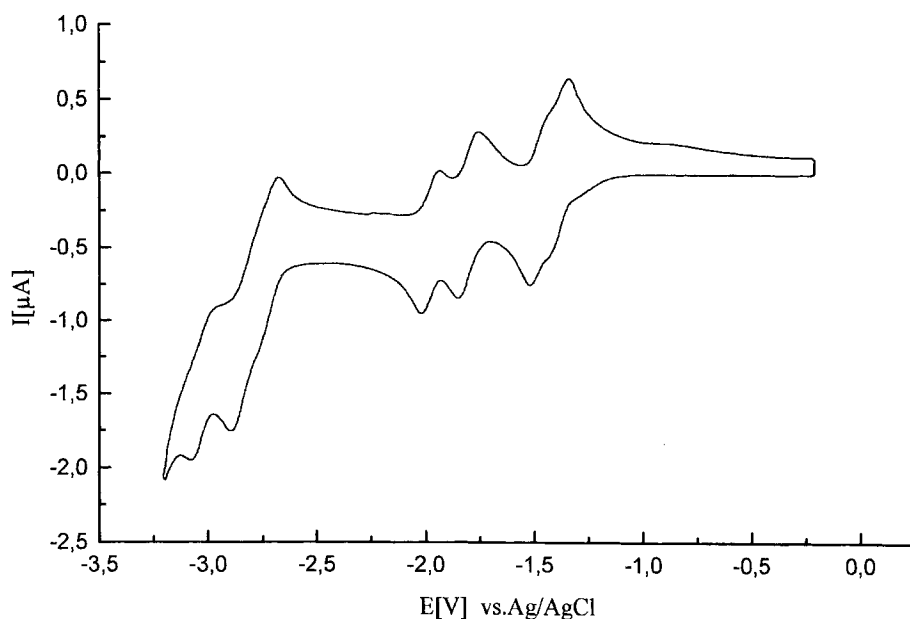


**Chart 13-3.** Structures of the starting materials **34**, **35**, and **36** for the synthesis of PAHs **37** and **38**.

**Table 13-4.** Redox potentials (V) versus Ag/AgCl of compounds **37** and **38**<sup>a</sup>.

	Reduction					Oxidation			
	$E_{1/2}^6$	$E_{1/2}^5$	$E_{1/2}^4$	$E_{1/2}^3$	$E_{1/2}^2$	$E_{1/2}^1$	$E_{1/2}^2$	$E_{1/2}^3$	$E_{1/2}^4$
<b>37</b>	-3.10 V	-2.92 V <sup>b</sup>	-2.00 V	-1.82 V	-1.50 V	-1.40 V	+0.89 V	+1.28 V	+1.54 V
<b>38</b>	-2.55 V	-2.42 V	-2.16 V	-2.04 V	-1.41 V <sup>b</sup>	-1.13 V <sup>b</sup>	+0.85 V	+1.21 V	+1.34 V

<sup>a</sup> The cyclic voltammograms were recorded in THF/TBAPF<sub>6</sub> (reductions) and CH<sub>2</sub>Cl<sub>2</sub>/TBAPF<sub>6</sub> (oxidations) at -40 °C (scan rate: 200 mVs<sup>-1</sup>; TBA = tetrabutylammonium); <sup>b</sup> Two-electron transfer steps.



**Figure 13-17.** Reduction part of the cyclic voltammogram of compound **38** in THF/TBAPF<sub>6</sub> at  $-40^{\circ}\text{C}$  (scan rate:  $200\text{ mV s}^{-1}$ )

## 13.6 Summary and Outlook

The DA reaction is a powerful tool for the synthesis of linearly and angularly annulated, double-stranded polymers. If this tool is to be exploited to its full potential, the bi-functional DA monomers need to be substituted with flexible chains. Together with the kinks in the polymer backbones, generated during the growth process, this is the essential means that keeps the polymers in solution, and thus accessible to further growth. The excellent solubility of the ladders enabled investigation of their structural characteristics in great detail, and profound knowledge is therefore now available not only on the repeat unit's constitution and the molecular weights, but also on stereochemical and shape aspects. Furthermore, the solubility allows processing of the higher molecular weight candidates into mechanically stable films, which, in the case of Group 3 polymer **20b**, was successfully used to

generate the fully unsaturated analog. Because of its sequence of six- and five-membered rings, this analog may be considered as a buckyball peel. Finally, it was briefly shown that DA methodology can also be successfully applied to the synthesis of extremely long, monodisperse polycyclic aromatic hydrocarbons.

DA ladder polymers provide a valuable addition to chemical and polymer chemical knowledge, in that they are the first rigorously proven examples of double-stranded polymers. All other polymers, including those in daily life, are single-stranded ones. This also holds true for biopolymers like RNA, DNA, or proteins that are only double-stranded in a formal sense. One of the strands is based on covalent, the other on hydrogen bonds. Future research towards interesting applications looks most promising in the field of electro-optics. Within the next few years, whether perfect ladder polymers with extended  $\pi$ -conjugation can be



converted into materials with useful applications will be known.

## 13.7 Acknowledgements

I would like to thank my co-workers for all the effort they invested in this project. Only through their hard, creative, and ambitious work could it be developed to its present near-ripe state. Their names can be found in the list of references. I also wish to thank my former mentor, Prof. G. Wegner (Mainz), for generating my interest in this area of synthetic chemistry, and for other support. Financial support was generously provided by the Bundesministerium für Forschung und Technologie, the Max Planck Society, Fonds der Chemischen Industrie, and Deutsche Forschungsgemeinschaft.

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# 14 Synthesis of Polyrotaxanes

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## List of Symbols and Abbreviations

$m$	number
$n$	number
$x/n$	threading efficiency
$T_g$	glass transition temperature
AIBN	2,2'-azobisisobutyronitrile
CD	cyclodextrin
CP	cross polarization
CPMAS	cross polarization/magic angle spinning
DMF	dimethyl formamide
DMSO	dimethylsulfoxide
DNP	dinitrophenyl
DP	degree of polymerization
DSC	differential scanning calorimetry
GPC	gel permeation chromatography
IR	infrared
Me	methyl
MT	molecular tube
MW	molecular weight
NMP	N-methylpyrrolidone
NMR	nuclear magnetic resonance
NOESY	nuclear Overhauser effect spectroscopy
OE	oligoethylene
OEG	oligo(ethylene glycol)
PEG	poly(ethylene glycol)
PEG-BA	poly(ethylene glycol)-bisamine
PEG-DNB2	bis(3,5-dinitrobenzoyl)-poly(ethylene glycol)
PEG-DNP2	bis(2,4-dinitrophenylamino)-poly(ethylene glycol)
PEG-1N2	bis(1-naphthylacetyl)-poly(ethylene glycol)
PEG-2N2	bis(2-naphthylacetyl)-poly(ethylene glycol)
PIB	polyisobutylene
PMeVE	poly(methyl vinyl ether)
PO <sub>x</sub>	poly(oxytrimethylene)
PPG	poly(propylene glycol)
PST MAS	pulse saturation transfer magic angle spinning
P (THF)	poly(tetrahydrofuran)
TEG	tetrakis(ethylene glycol)
TFA	trifluoroacetyl
THF	tetrahydrofuran
TNBS	trinitrobenzene sulfonic acid
UV	ultraviolet
VLSI	very large scale integrated

## 14.1 Introduction

In recent years, much attention has been directed toward the construction of micrometer to nanoscale architectures from bulk materials by top down engineering as exemplified by the production of VLSI (very large scale integrated) systems. However, there is a limit to “top down” approaches for various reasons, including the interference of light waves for lithography (Philp and Stoddart, 1996). Hence, “bottom up” procedures from a molecule to create new architectures have become an important approach. This approach is used by Nature itself. Most of the structures of biological systems have been made by the self-assembly and self-organization of specific molecules.

Inclusion compounds are some of the most important molecular self-assemblies made of synthetic molecular parts (Harada, 1996 a). Urea, thiourea, and deoxycholic acid are frequently used as host molecules for small guest molecules. Inorganic compounds, such as zeolites and clays, are also used as hosts for guests to form inclusion compounds.

Polymer blends, alloys, and composites have been studied by mixing polymers of different species. However, in this case, the structures and properties are statistical in nature. Polymers have a lot of information in their main chains and side chains. If polymers are able to be used as guest molecules, the resultant complexes should have new structures and functions. Polymeric inclusion compounds are thought to be a typical example of nanoscale composites, i.e., molecular level composites made by bottom up approaches.

More recently, with the advent of host-guest chemistry, the chemistry of molecular recognition, and supramolecular science, polymeric inclusion compounds have at-

tracted attention, not only due to their unique structures, but also due to their construction of polymeric assembly materials and more complex systems with unique properties and functions.

In this review, the design and preparation of polyrotaxanes are described. Rotaxanes and catenanes containing other ring components are also reviewed.

## 14.2 Rotaxanes and Catenanes

In recent years, much attention has been focused on supramolecular science, the science of noncovalent assembly, because of the recognition of the importance of specific noncovalent interactions in biological systems and in chemical processes (Lehn, 1992). Rotaxanes, from the Latin *rota* meaning wheel, and *axis* meaning axle, make up one of the classical classes of molecules consisting of a dumbbell-shaped component, in the form of a rod, and two bulky stopper groups, around which there are encircling macrocyclic component(s) (Schill, 1971) (Fig. 14-1). Catenanes make up a series of molecules with two or more interlocking rings which are not chemically bound to each other. Rotaxanes and catenanes have been synthesized in a statistical way; thereby, the yields were very low (Agam et al., 1976; Harrison and Harrison,

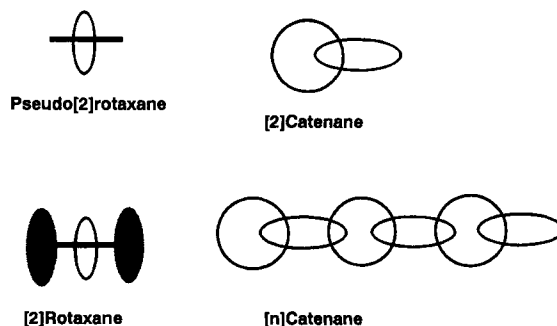


Figure 14-1. Rotaxanes and catenanes.

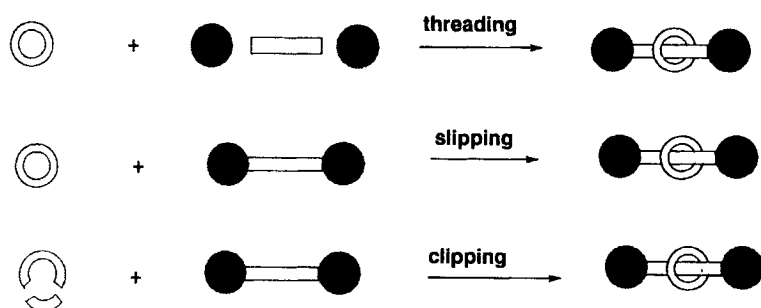


Figure 14-2. Synthesis of rotaxanes and catenanes.

1967; Harrison, 1972). Recently, rotaxanes and catenanes have attracted renewed interest in the field of supramolecular chemistry, because of their unique structures and properties. Rotaxanes can be prepared by closing the end groups of the “axle” by means of large groups within the ordered environments of the noncovalent templating forces, in such a way as to retain the order originally imposed by the weak interactions (Anelli et al., 1990). By this method, rotaxanes and catenanes containing crown ethers, cyclobis(paraquat-*p*-phenylene), and cyclodextrins have been synthesized in high yields. Not only rotaxanes and catenanes, but polyrotaxanes have also been prepared, and polycatenanes are becoming the new target (Fig. 14-2). This chapter describes the preparation, structures, and some properties of such rotaxanes and catenanes.

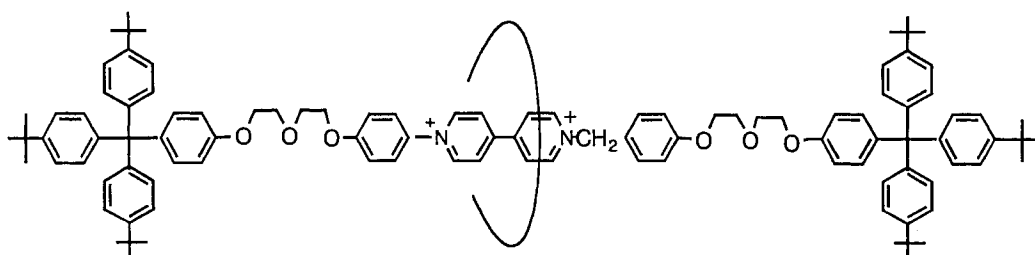
### 14.2.1 Rotaxanes

#### 14.2.1.1 Preparation of Rotaxanes

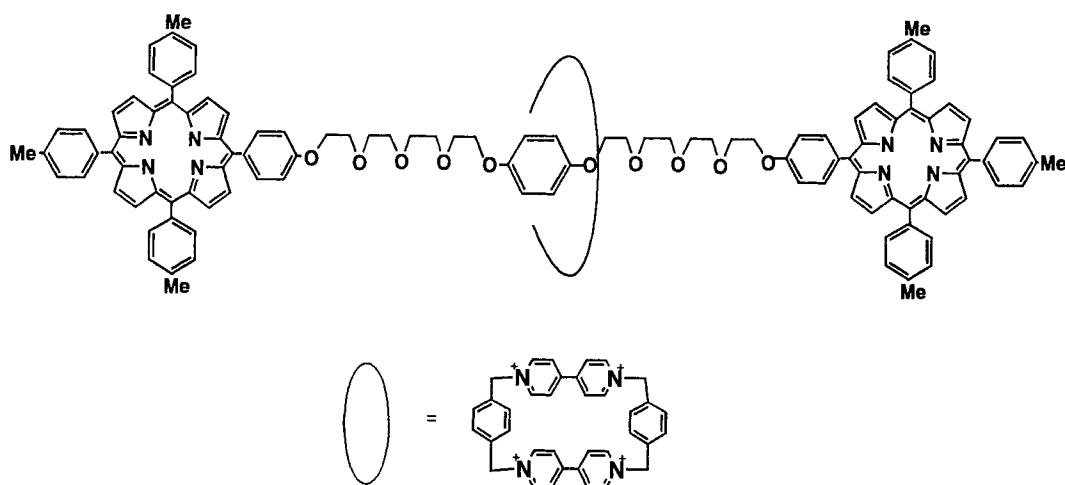
Rotaxanes are compounds in which rings are threaded by a chain. If both ends of the chain are not blocked by bulky substituents, they are called “pseudo-rotaxanes”, because they dissociate into each component under certain conditions. If both ends are blocked by large substituents and imprisoned rings cannot escape from the molecule, they are called “rotaxanes”. A rotaxane containing a

single ring is called [2]rotaxane and one containing  $n$  rings is called [ $n$ ]rotaxane.

Stoddart and coworkers found that bis-*p*-phenylene-34-crown-10 forms a one-to-one inclusion complex with paraquat (Allwood et al., 1987) and 4,4'-bipyridinium dication derivatives with long chains (Ashton et al., 1991 a), in which the substituents on the bipyridine nitrogen atoms are, respectively, 2-hydroxyethyl and 2-(2-hydroxyethoxy)-ethyl groups to give pseudo-rotaxanes. Recently, they obtained [2]rotaxanes by slip-page reactions of the crown compound into the dumbbell component, in which large stoppers are attached on both ends of the axle molecule (Ashton et al., 1993 a, b) (Fig. 14-3). They also found that cyclobis(paraquat-*p*-phenylene) forms inclusion complexes with dimethoxybenzene and dimethoxynaphthalene (Odel et al., 1988; Ashton et al., 1988; Reddington et al., 1991). On the basis of this finding, they succeeded in obtaining pseudo-rotaxane by introducing hydroquinone derivatives containing polyether chains into cyclobis(paraquat-*p*-phenylene) (Anelli et al., 1991 a). They have obtained [2]rotaxanes by attaching bulky substituents, such as triisopropyl silyl groups, at each end of the complex (Anelli et al., 1990). They also prepared pseudo-rotaxanes containing two cyclobis(paraquat- $\pi$ -phenylene)s threaded by a long polyether chain (Ashton et al., 1991 b). Stoddart also obtained a [2]rotaxane using porphy-



**Figure 14-3.** [2]Rotaxane consisting of bis-*p*-phenylene-34-crown-10 and a 4,4'-bipyridinium dication derivative.



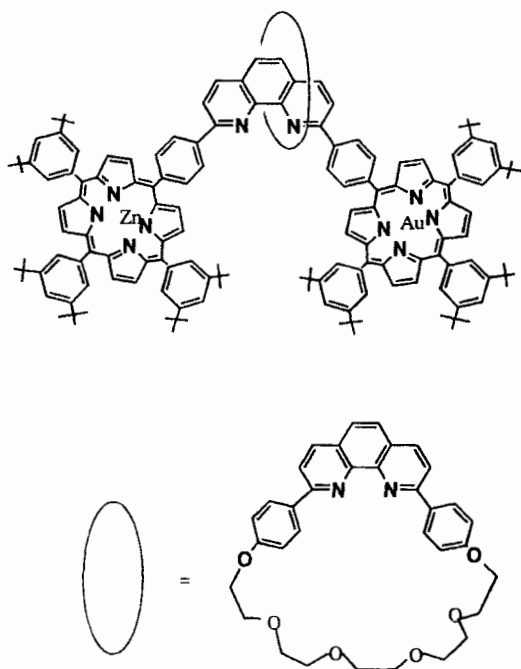
**Figure 14-4.** [2]Rotaxane containing porphyrins as stoppers.

rins as stoppers (Ashton et al., 1992 b) (Fig. 14-4). Sauvage reported a rotaxane with two rigidly held porphyrins as stoppers obtained by a copper(I)-based template strategy (Chambron et al., 1992) (Fig. 14-5).

Stoddart and co-workers prepared a rotaxane with two “stations” which have some interactions with cyclobis (paraquat-*p*-phenylene) (Anelli et al., 1991 b) (Fig. 14-6). The  $^1\text{H}$  NMR spectra of the compound at room temperature show that the ring molecule moves to and fro like a molecular “shuttle” about 500 times a second between the two stations. Similarly, they prepared a

[2]rotaxane consisting of two bipyridinium units and crown beads (Ashton et al., 1992 a; Ballardini et al., 1993). It is of interest whether such movements can be controlled by light or an electrochemical method (Beniston and Harriman, 1993). Kaifer and co-workers prepared a molecular shuttle containing both a benzidine unit and a bisphenol unit in the axle (Bissell et al., 1994). In this compound, 86% of the tetracation beads exist at the benzidine side at 229 K (Fig. 14-7). However, when the compound was treated with acid or oxidized electrochemically, the beads could be moved successfully to the biphenol side.



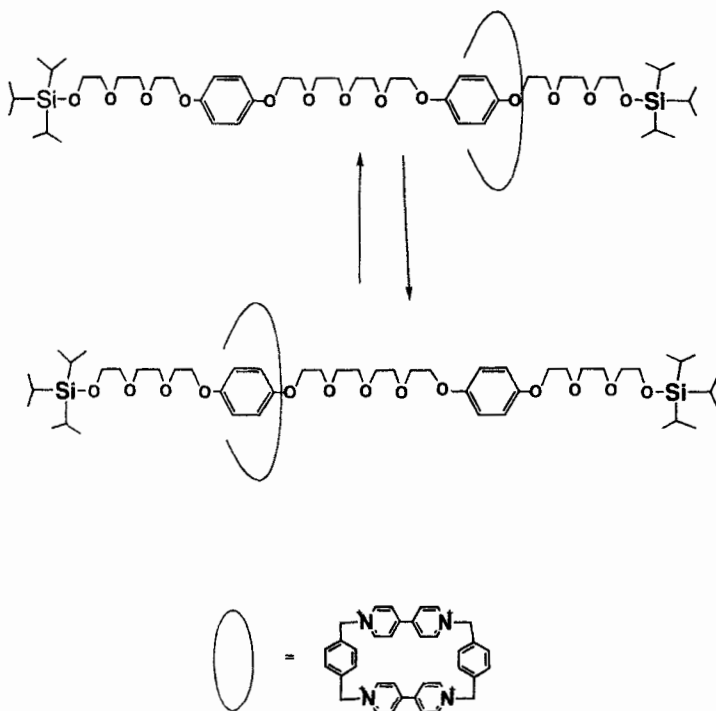


**Figure 14-5.** [2]Rotaxane containing porphyrins as stoppers.

#### 14.2.1.2 Rotaxanes Containing Cyclodextrin

Cyclodextrins are a series of cyclic oligosaccharides consisting of six to eight glucose units linking through  $\alpha$ -1-4, glycosidic linkages (Fig. 14-8). They are called  $\alpha$ -,  $\beta$ -, and  $\gamma$ -cyclodextrin (CD), respectively. They are known to form inclusion complexes with a wide variety of low molecular weight compounds, ranging from nonpolar hydrocarbons to polar carboxylic acids and amines. There have been some reports on the preparation of rotaxanes containing CDs.

[2]Rotaxanes containing cyclodextrin and its derivatives as beads have been reported (Stoddart, 1992). Ogino and co-workers reported [2]rotaxanes containing cobalt complexes as stoppers (Ogino, 1981; Ogino and Ohata, 1984) (Fig. 14-9). Lawrence and co-workers reported [2]rotaxanes



**Figure 14-6.** Molecular shuttle using cyclobis(paraquat-*p*-phenylene) ring.

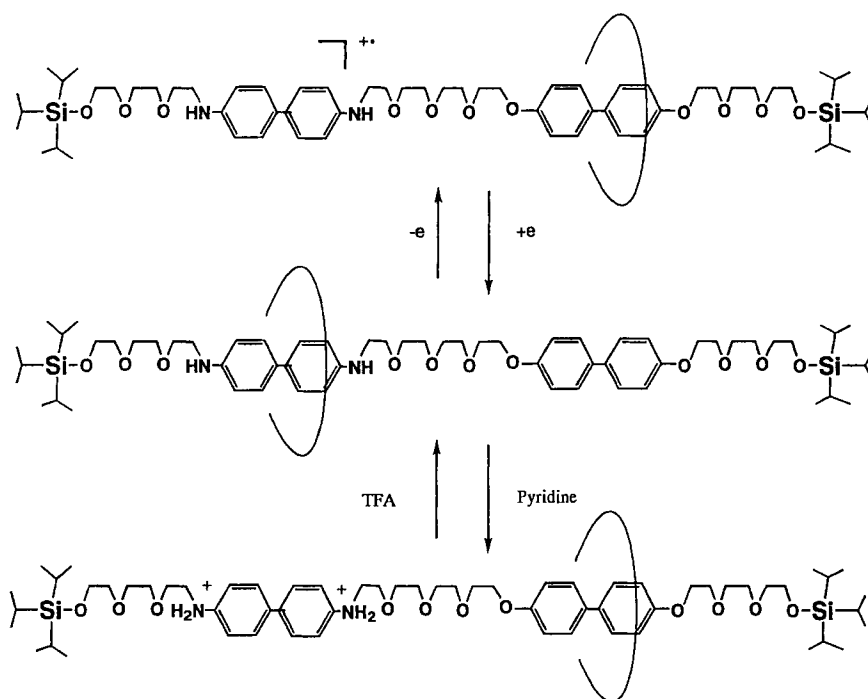


Figure 14-7. A chemically and electrochemically switchable molecular shuttle.

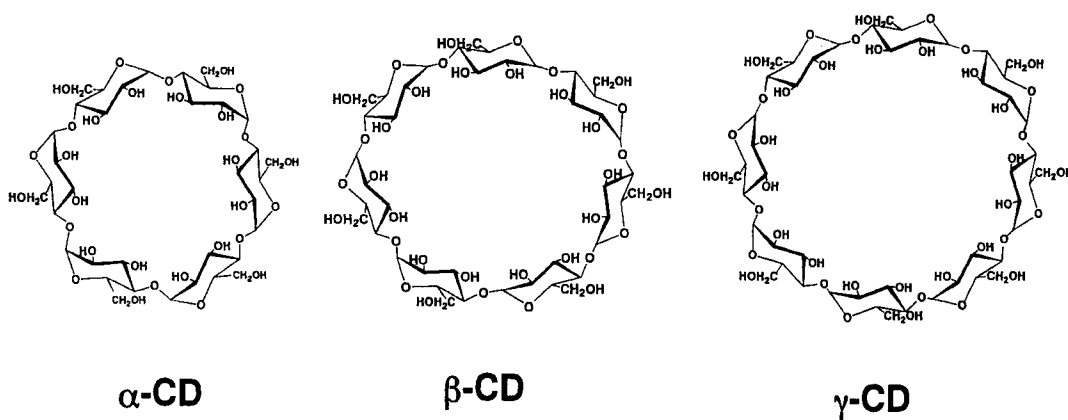


Figure 14-8. Structures of  $\alpha$ -,  $\beta$ - and  $\gamma$ -cyclodextrins.

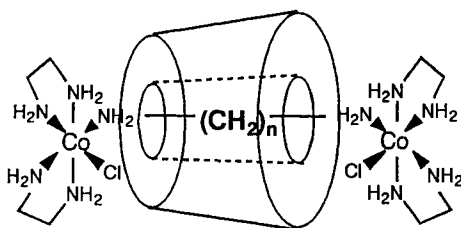
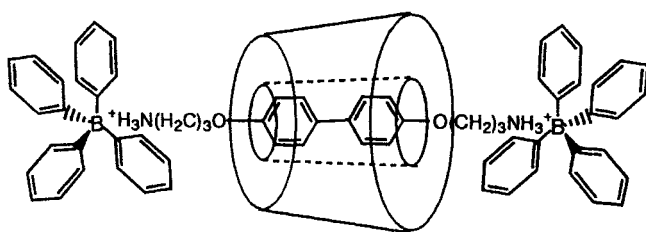
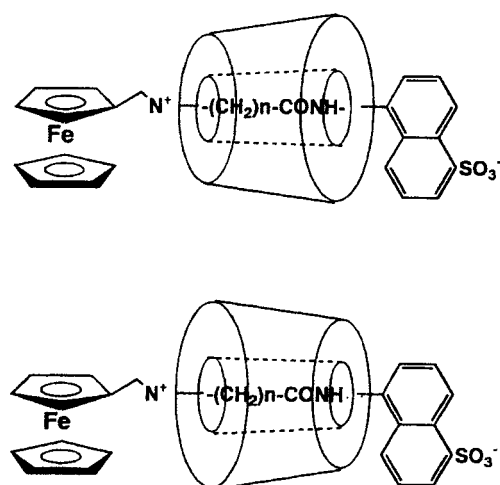


Figure 14-9. [2]Rotaxane containing cobalt complexes as stoppers.

containing biphenyls or porphyrins as axles and dimethyl  $\beta$ -cyclodextrin as beads (Manka and Lawrence, 1990; Rao and Lawrence, 1990, Dick et al., 1992) (Fig. 14-10). Kaifer and co-worker prepared asymmetric [2]rotaxanes consisting of ferrocenes and naphthalene sulfonate as stoppers (Ishnin

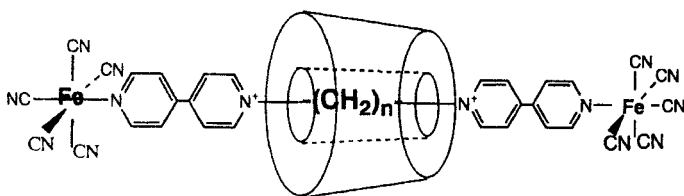


**Figure 14-10.** [2]Rotaxane containing biphenyl and dimethyl  $\beta$ -CD.

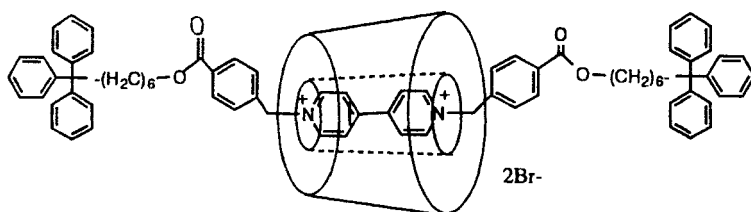


**Figure 14-11.** Asymmetric [2]rotaxane consisting of ferrocenes and  $\alpha$ -CD.

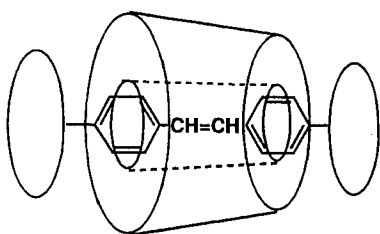
and Kaifer, 1991) (Fig. 14-11). Macartney and co-worker obtained symmetric [2]rotaxanes using pentacyanoiron complexes as stoppers and  $\alpha$ -CD as a bead (Wylie and Macartney, 1992) (Fig. 14-12). Wenz et al. (1992) obtained a hydrophobic [2]rotaxane containing bipyridinium (Fig. 14-13). Nakashima and co-workers reported a [2]rotaxane of  $\beta$ -CD threaded by a 4,4'-diaminostilbene (Kunitake et al., 1993) (Fig. 14-14). Harada et al. (1996b) first prepared a nonionic neutral [2]rotaxane containing a cyclodextrin derivative using trinitrobenzene derivatives as stoppers (Fig. 14-15).



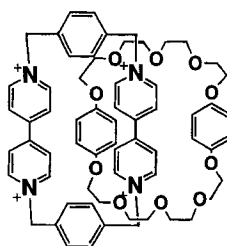
**Figure 14-12.** Symmetric [2]rotaxane using a pentacyanoiron complex.



**Figure 14-13.** Hydrophobic [2]rotaxane containing bipyridinium.



**Figure 14-14.** [2]Rotaxane consisting of 4,4'-diaminostilbene and  $\beta$ -CD.



**Figure 14-16.** [2]Catenane consisting of bis(bipyridyl) and crown ether.

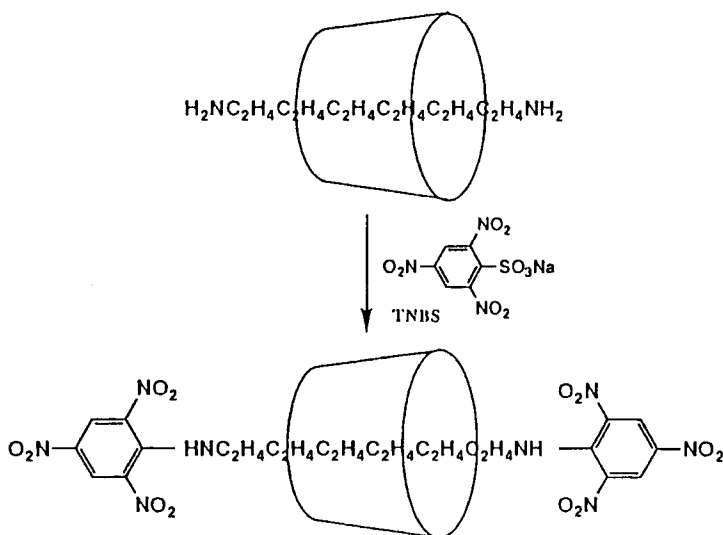
## 14.2.2 Catenanes

### 14.2.2.1 Preparation of Catenanes

“Catenane” stems from the Latin word *catena* meaning chain. A catenane consisting of two rings is called [2]catenane and one containing  $n$  rings is named [ $n$ ]catenane. Catenanes have been prepared by “clipping” a ring molecule. However, since this method is of a statistical nature, the yields of the products are extremely low (less than 0.001%) (Frisch and Wasserman, 1961). The difficulty is that the threading should be conducted in a condensed phase, but clipping should be done in dilute solution so as not to result in oligomer/polymer

formation. In order to overcome this difficulty, specific weak intermolecular interactions between its precursors (host-guest interactions), a ring and an axle, have been successfully applied to the synthesis of many catenanes. Recently, many catenanes were successfully prepared in high yields by this method.

Stoddart and co-workers prepared [2]catenanes by the cyclization reaction of bis(bipyridyl)s in the presence of crown ethers in 70% yield (Ashton et al., 1989, 1991a, 1994; Amabilino et al., 1993) (Fig. 14-16). The high yield is due to a  $\pi$ -donor-acceptor interaction between the ring and the thread. The ring molecule of this compound was found to rotate around an-



**Figure 14-15.** Neutral [2]rotaxane using trinitrobenzene as stoppers.

other ring. [3]Catenanes (Ashton et al., 1991b) (Fig. 14-17), [4]catenanes (Amabilino et al., 1994a), and [5]catenanes (Amabilino et al., 1994b), which have three, four, or five rings in the molecule, respectively, have been reported. Recently, Stoddart and co-workers succeeded in the preparation of a [5]catenane, that has a structure similar to the symbol of the International Olympics (Fig. 14-18). The [5]catenane was named "olympiadane".

#### 14.2.2.2 Catenanes Containing Metal Complexes

Sauvage prepared various [2]catenanes using transition metal complexes as templates (Chambron et al., 1993) (Fig. 14-19). They also obtained [*n*]catenanes, in which many rings are interlocked with each other,

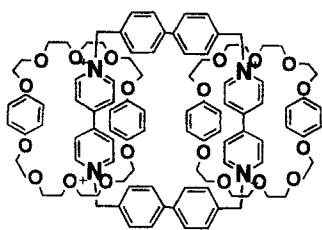


Figure 14-17. [3]Catenane.

and even a trefoil in which a ring is entangled by a similar procedure (Buchecker et al., 1990). Sauvage also obtained multi-ring catenanes using metal complexes as templates (Bitsch et al., 1991). Fujita et al. (1994) obtained a [2]catenane containing a cyclic palladium complex by a clipping method.

#### 14.2.2.3 Catenanes Containing Cyclodextrin

In 1958, Cramer and co-workers tried to prepare a [2]catenane by clipping a dithiol thread penetrating a CD ring by oxidation (Lüttringhus et al., 1958) (Fig. 14-20). But they could not obtain [2]catenanes. Stoddart and co-workers obtained a [2]catenane by threading a biphenyl derivative into a  $\beta$ -CD and clipping the thread (Armspach et al., 1993) (Fig. 14-21). Harada et al. (1996d) also obtained [2]catenanes by threading a methylene chain and cyclizing with oligo-ethylene glycol derivatives (Fig. 14-22).

#### 14.2.2.4 Other Catenanes

Vögtle prepared [2]catenanes containing cyclic lactams in high yields (Vögtle et al., 1992). They also obtained [2]catenane con-

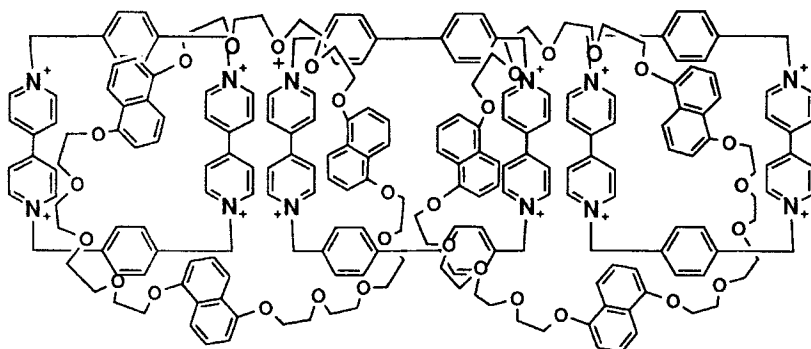
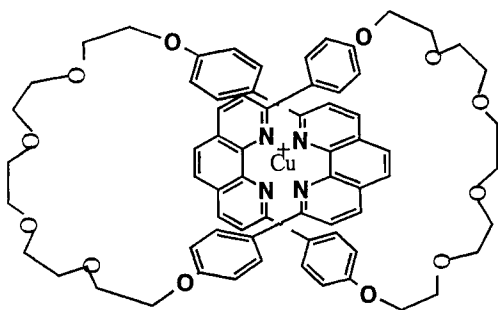
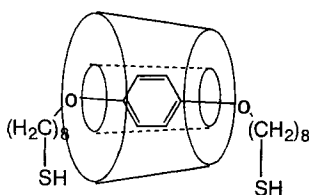


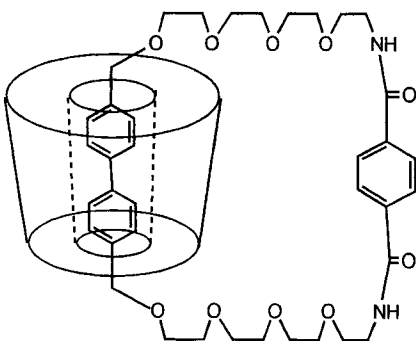
Figure 14-18. [5]Catenane olympiadane.



**Figure 14-19.** [2]Catenane prepared using a transition metal complex as the template.

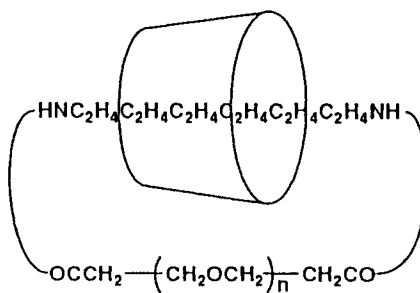


**Figure 14-20.** [2]Catenane precursor containing CD and a dithiol thread.



**Figure 14-21.** [2]Catenane consisting of a biphenyl derivative and  $\beta$ -CD.

taining an azobenzene moiety and found that the movement of the ring can be controlled by light (Vögtle et al., 1993). Catenanes consisting of bipyridinium cyclophanes and porphyrins have been reported (Gunter and Johnston, 1992).



**Figure 14-22.** [2] Catenane consisting of methyl  $\beta$ -CD, oligoethylene, and oligoethylene glycol.

## 14.3 Main Chain Polyrotaxanes

There are two types of polyrotaxanes: main chain and side chain polyrotaxanes (Gibson and Marand, 1993). Figure 14-23 shows a schematic illustration of polyrotaxanes. There are two types of main chain polyrotaxanes: a [2]rotaxane polymer and a polymer in which many ring molecules are threaded.

There are many types of combinations of macrocycles and linear polymer constituents. A wide variety of physical properties can be achieved by a combination of macrocycles and a polymer. For example, the crystallinity, glass transition temperature, toughness, and solubility of polymers could be changed by forming polyrotaxanes with cyclic molecules.

There are two main approaches to synthesize polyrotaxanes: the "statistical" and the "template" approaches mentioned earlier for the synthesis of rotaxanes and catenanes. There are some methods to obtain main chain polyrotaxanes. Threading is frequently used for this purpose. The polymerization of monomeric rotaxanes, the production of linear macromolecules in the presence of macrocycles, and cyclization in the presence of macromolecules (clipping) are also used for the synthesis.

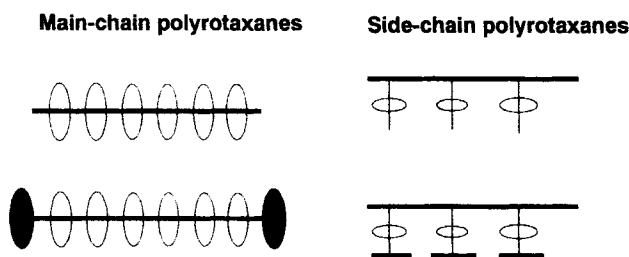


Figure 14-23. Polyrotaxanes.

### 14.3.1 Crown Ethers

Polyrotaxanes were prepared for the first time by Agam et al. (1976) from crown ethers and oligoethylene glycols. Oligo(ethylene glycol)s were equilibrated with crown ethers and then naphthalene-1,5-diisocyanate was added to the mixture to form polyurethane. Later, Gibson and co-worker prepared polyrotaxanes containing crown ethers and polymers of various kinds (Gibson and Engen, 1994).

#### 14.3.1.1 Polyesters

Gibson and Engen (1994) prepared poly-[(alkylene sebacate)-rotaxa-(crown ether)]s from sebacoyl chloride and alkanediols using crown ethers as solvents (Fig. 14-24). The diols were equilibrated with the crown ether to form rotaxane, and then the diacid chloride was added. The products were purified and characterized as follows: The reaction mixture was added to a good solvent of the crown ethers which was a nonsolvent for the polymer. This method was repeated until a constant composition, which was determined by NMR measurements, was reached. Usually, only two precipitations of

the product are enough to remove non-threaded crown ethers. GPC was used to confirm the absence of nonthreaded crown ethers. The topology was further demonstrated by recovering the crown ether after hydrolysis of the polymer chain.

At first, Gibson and Engen reported condensation of sebacoyl chloride with 1,10-decanol in the presence of 30-crown-10, followed by the addition of triphenylpropionyl chloride, to give a low molecular weight polyrotaxane. Transesterification of dimethyl sebacate with triethylene glycol in the presence of the crown ethers, followed by the addition of a triarylmethane for the blocking groups, is more efficient (Wu et al., 1991). One crown ether was incorporated for every four monomer units in the poly(triethylenoxy sebacate) backbone. A molecular weight of about 11 000–12 200 was obtained and about 25% of the polymer chain was encircled by the macrocycle. The polyrotaxane is an oil, whereas the polymer is a solid. This result indicates that the crown ether is either a solvent or a plasticizer. In these cases, bulky end stoppers are not always necessary, even for relatively low molecular weight polymers. Coiling of the polymer chain and the crown ethers prevents dethreading in solution and melting over several days.

The equilibrium constant for the threading of 42-crown-14 into the polyester is independent of the chain length, suggesting that the formation of rotaxanes is promoted by the formation of hydrogen bonding

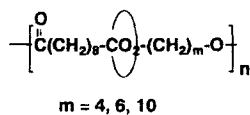


Figure 14-24. Polyester rotaxane.

between the terminal hydroxyl groups and the crown ethers.

The threading efficiency ( $x/n$ , i.e., the value of the average number of cyclic molecules threaded onto each repeat unit) greatly increases as the ring size increases. The solubilities of polyrotaxanes are enhanced relative to those of the parent polymers. The polyrotaxane of poly(butylene sebacate) with 60-crown-20, for example, is soluble in methanol, although the backbone polyester is insoluble in methanol.

The polymer morphology of polyrotaxanes was found to be different from that of the corresponding blends. The crystallization of the polyrotaxane was followed by DSC. Upon cooling from the melt, the polyester component crystallized first, while the crown ether crystallized at a lower temperature.

Polyester rotaxane, ( $n/x=79$ ) containing 4 mass % cyclic exhibited an intrinsic viscosity in  $\text{CHCl}_3$  of twice that of the parent polyester. This result indicates that the threading of a single crown ether on a polymer chain on average doubles the hydrodynamic volume. GPC experiments showed similar results.

#### 14.3.1.2 Polyurethanes

Gibson and co-workers prepared a series of polyurethane rotaxanes from tetraethylene glycol and bis(*p*-isocyanatophenyl)methane using various crown ethers (Shen et al., 1994) (Fig. 14-25). The polyrotaxanes were prepared by condensation using crown ethers as solvents. The glycol and the crown ether were mixed and stirred in the melt for 1 h before the isocyanate was added. The polyrotaxanes were purified by reprecipitations from THF into methanol, water, ethyl acetate, or mixed solvents. In spite of the fact that there were no bulky stoppers at the ends of the polyrotaxanes,

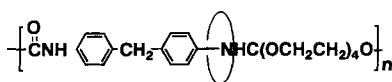


Figure 14-25. Polyurethane rotaxane.

the macrocycles did not come off. One of the reasons for the lack of dethreading in solution is coiling of the chains and the formation of hydrogen bonds between macrocycles and a polymer chain. The “wobble effect” of the chain ends as a result of enhanced mobility relative to the middle of the chain might force the macrocycles away from the chain ends and towards the middle.

The threading efficiency ( $x/n$ ) increases with increasing ring size at a constant cyclic to linear unit ratio. The amount of threading increases with the feed ratio of macrocycle to glycol, suggesting that the phenomenon follows Le Chatelier's principle. Equilibrium constants increase with increasing ring size. For flexible rings, the ratio of threadable to unthreadable rings is thought to be an exponential of the ring size.

Polyurethane is insoluble in water and acetone. However, polyrotaxanes are soluble in acetone, and in some cases soluble in water. The glass transition temperature ( $T_g$ ) is proportional to the mass fraction of macrocycle. The polyrotaxanes behave as a corresponding blend. When the mass fraction of crown ether is large, the crown ether can crystallize without dethreading.

#### 14.3.1.3 Polyaramides

Gibson and Marand (1993) prepared polyaramide rotaxanes from isophthalic acid and bis(*p*-aminophenyl)ether using 30-crown-10 and 60-crown-20 (Fig. 14-26). DSC studies showed that in solution the crown ethers formed hydrogen bonds with the amide linkages. This interaction is con-



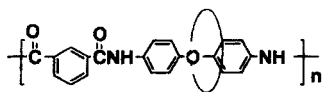


Figure 14-26. Polyaramide rotaxane.

served in the solid state. IR studies show that there are nonhydrogen-bonded amide carbonyl absorptions in fresh samples and hydrogen-bonded carbonyls in polyamides.

#### 14.3.1.4 Bipyridinium Polymers

Shen et al. (1992) prepared a series of polyurethane rotaxanes based on poly(tetramethylene oxide), bis(*p*-isocyanatophenyl)methane, *N,N'*-bis(2-hydroxyethyl)-4,4'-bipyridinium hexafluorophosphate and bis(*p*-phenylene)34-crown-10. The bipyridinium group and the crown ether form inclusion complexes to form rotaxane monomer. The  $^1\text{H}$  NMR spectrum of the complex showed that there are distinct NMR shifts at the aromatic signals and the bipyridinium units. About 45% of the bipyridinium sites were occupied by crown ethers.

#### 14.3.1.5 Polystyrenes and Polyacrylonitriles

Engen, Lee, and Gibson reported that free-radical polymerization with AIBN yielded a family of polystyrene-based rotaxanes and the corresponding polyacrylonitrile-based rotaxane using various crown ethers as solvents (Gibson and Engen, 1993) (Fig. 14-27). They used azo initiator containing triarylalkyl moieties to attach stop-

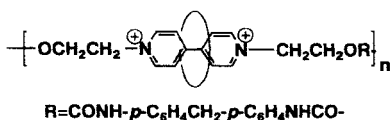


Figure 14-27. Polybipyridyl rotaxane.

pers at the ends. The extent of macrocycle can be controlled by varying the feed ratio.

Gibson and co-worker reported that anionic polymerization gave poly[(styrene)-rotaxa-(30-crown-10)] (Gibson and Engen, 1994). The threading efficiency was a function of solvent, temperature, and concentrations, but, at a low temperature in THF, anionic polymerization resulted in a higher cyclic incorporation than the free-radical approach. This is, according to the authors, presumably due to complexation of the crown ethers with  $\text{Na}^+$  counterions. Polystyrene rotaxanes behave surfactant-like. They show two  $T_g$ s at  $-14^\circ\text{C}$  and  $104^\circ\text{C}$ , while crown ether has a  $T_g$  of  $-15^\circ\text{C}$  and the polymer has a  $T_g$  of  $98^\circ\text{C}$ . Phase mixing does not seem to occur.

Although polyacrylonitrile is only soluble in DMF, NMP, etc., poly(acrylonitrile/rotaxane) was completely soluble in methanol.

#### 14.3.2 Cyclodextrins

Cyclodextrins are known to form inclusion complexes with various compounds. However, studies on the inclusion properties of cyclodextrins were limited to those of low molecular weight compounds (Bender and Komiyama, 1978; Szejtli, 1982). There were no reports on the complex formation of cyclodextrins with polymers when we started our work in the early 1980s.

We found that cyclodextrins form complexes with various polymers with high specificities to give crystalline complexes in high yields (Harada, 1993; Harada et al., 1993 a). Polyrotaxanes in which many CD rings are entrapped are formed by capping the chain with bulky end groups (Harada et al., 1992, 1993 c). Tubular polymers were prepared from the polyrotaxanes.

### 14.3.2.1 Poly(ethylene glycol)

When aqueous solutions of PEG were added to a saturated aqueous solution of  $\alpha$ -CD at room temperature, the solution became turbid and the complexes were formed as precipitates (Harada and Kamachi, 1990 a; 1993 b).

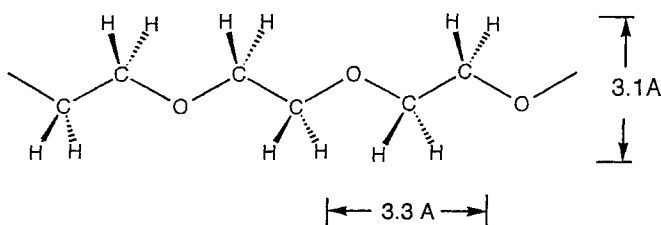
The complexes were isolated by filtration or centrifugation.  $\alpha$ -CD did not form complexes with the low molecular weight analogs, ethylene glycol, diethylene glycol, and triethylene glycol under the same conditions.  $\alpha$ -CD formed complexes with PEG of molecular weight higher than 200. The yields increased with an increase in the molecular weight. The complexes were obtained almost quantitatively with PEG of molecular weight over 1000.  $\beta$ -CD did not

form complexes with PEG of any molecular weight. This finding that a minimum PEG length is required for the formation of stable cyclodextrin complexes shows the importance of cooperativity in complexation.

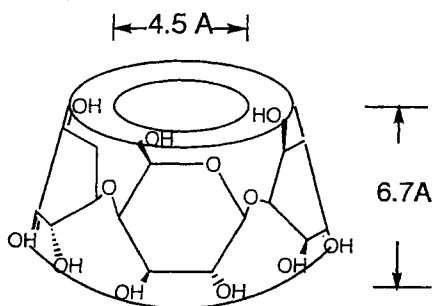
The continuous variation plots for the complexation between  $\alpha$ -CD and PEG and the  $^1\text{H}$  NMR spectra showed that the stoichiometries of the complexes are 2:1. The stoichiometries of the complexes are always 2:1, even if  $\alpha$ -CD and PEG are combined in any ratios. The length of two ethylene glycol units [6.6 Å (0.66 nm)] is similar to the depth of the cavity of  $\alpha$ -CD [6.7 Å (0.67 nm)] (Fig. 14-28).

The structures of the inclusion complexes of CDs with low molecular weight compounds can be classified into two groups:

PEG(Polyethylene glycol)



$\alpha$ -CD



**Figure 14-28.** Poly(ethylene glycol) and  $\alpha$ -CD.

“cage type” and “channel type”. The X-ray pattern of the  $\alpha$ -CD-PEG complex shows that the complexes are crystalline, and the patterns are similar to those of the complex with a channel structure, but different from those of the complexes with a cage type structure. These results indicate that the complexes of  $\alpha$ -CD and PEG have a channel structure. Molecular models show that PEG chains are able to penetrate  $\alpha$ -CD cavities, while the poly(propylene glycol) chain cannot pass through the  $\alpha$ -CD cavity. These views are in accordance with our results that  $\alpha$ -CD formed complexes with PEG; but not with poly(propylene glycol).  $\beta$ -CD did not form complexes with PEG. A PEG chain is too thin to fit in the  $\beta$ -CD cavity. However,  $\beta$ -CD forms complexes with poly(propylene glycol). Model studies indicate that the  $\alpha$ -CD cavity [depth 6.7 Å (0.67 nm)] accommodates two ethylene glycol units [6.6 Å (0.66 nm)].

The  $^{13}\text{C}$  CPMAS NMR spectrum of  $\alpha$ -CD shows resolved C-1 and C-4-resonances from each of the six  $\alpha$ -1,4-linked glucose residues. In particular, the C-1 and C-4 adjacent to a conformationally strained glycosidic linkage are observed at 80 and 98 ppm, respectively. In the spectrum of the polyrotaxane, the peaks at 80 and 98 ppm disappeared and each carbon of the glucose was observed in a single peak. These results indicate that  $\alpha$ -CD assumes a symmetrical conformation and each glucose unit of CD is in a similar environment. The X-ray studies of single crystals showed that  $\alpha$ -CD assumes a less symmetrical conformation when it does not include guests in the cavity, and  $\alpha$ -CD adopts a symmetrical conformation when it includes guests in the cavities. CPMAS NMR spectra of complexed and uncomplexed CDs are consistent with the results by X-ray studies.

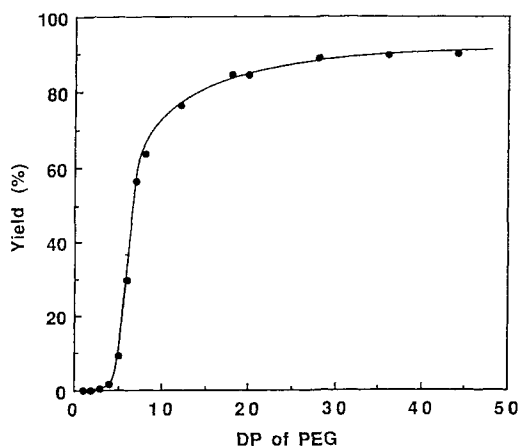
The polyrotaxanes of  $\alpha$ -CD with PEG of molecular weight less than 2000 are crystal-

line. The polyrotaxanes of  $\alpha$ -CD with PEG of low molecular weight (1000) are soluble in water, and those of higher molecular weight are solubilized by heating or on the addition of an excess amount of low molecular weight guests, such as benzoic acid, propionic acid, and propanol, to the suspension. The addition of urea, which is thought to affect hydrogen bonds, results in solubilization of the polyrotaxanes. The results indicate that hydrogen bonding plays an important role in forming the polyrotaxanes between PEG and  $\alpha$ -CD.

The decomposition point of the polyrotaxane is a little higher than that of the cyclodextrin. The polyrotaxane with PEG-1000 decomposes above 300 °C, whereas  $\alpha$ -CD melts and decomposes below 300 °C. Thus poly(ethylene glycol) stabilizes  $\alpha$ -CD.

The polyrotaxanes obtained from commercially available PEGs were polydisperse and heterogeneous. In order to make clear the chain-length selectivity and obtain pure monodisperse polyrotaxanes, we prepared monodisperse oligo(ethylene glycol)s (OEGs) and studied the interactions between  $\alpha$ -CD and the pure oligo(ethylene glycol)s.

Figure 14-29 shows the yields of the polyrotaxanes of  $\alpha$ -CD with OEG as a function of the degree of polymerization of OEG (Harada et al., 1994a). The yields are calculated on the basis of 2:1 stoichiometry. Complexes were not obtained with ethylene glycol, bis(ethylene glycol), and tris(ethylene glycol).  $\alpha$ -CD formed complexes with tetrakis(ethylene glycol) (TEG) and larger OEG, and the yields increased sharply with an increase in the degree of polymerization from 5 to 12. The polyrotaxanes were obtained almost quantitatively with eicosakis(ethylene glycol) and larger OEG.  $\beta$ -CD did not give polyrotaxanes with any OEG. The stoichiometries of the polyrotaxanes are 2:1 (two ethylene glycol units and one



**Figure 14-29.** Yields of the complexes of  $\alpha$ -CD with OEG as a function of the degree of polymerization.

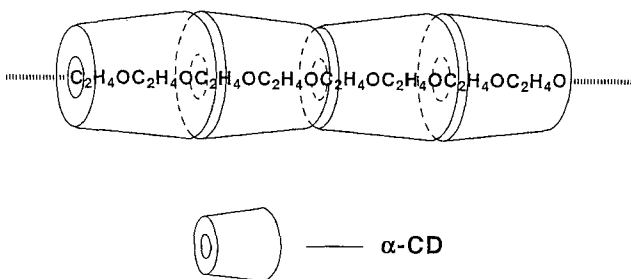
$\alpha$ -CD) when the degree of polymerization is higher than 6.

Cyclic oligomers of ethylene glycol (crown ethers, 15-crown-5 and 18-crown-6) did not form complexes with  $\alpha$ -CD. These crown ethers are too large to fit in the CD cavity and  $\alpha$ -CDs are not able to penetrate the chain due to the absence of the chain ends.  $\alpha$ -CD includes linear oligo(ethylene glycol) from small end groups.

PEGs with small end groups, such as methyl, dimethyl, and amino groups, form polyrotaxanes. PEG carrying bulky substituents, such as a 3,5-dinitrobenzoyl group and a 2,4-dinitrophenyl group at both ends of the PEG, which do not fit or pass through the  $\alpha$ -CD cavity, did not form any polyrotaxanes with  $\alpha$ -CD.

Figure 14-30 shows a proposed structure of a polyrotaxane consisting of poly(ethylene glycol) and  $\alpha$ -CD. The polyrotaxane formation from PEG and  $\alpha$ -CD is entropically unfavorable. However, formation of the complexes is thought to be promoted by hydrogen bond formation between neighboring cyclodextrins. Therefore a head-to-head and tail-to-tail arrangement is thought to be the most probable structure. A secondary hydroxy group side is called the "head" and a primary hydroxy group side is called the "tail". This structure was confirmed by X-ray crystallographic studies of a single crystal of the complex between  $\alpha$ -CD and hexaethylene glycol.

During the preparation of polyrotaxanes of CDs with PEG, we found that  $\gamma$ -CD formed a trace amount of complexes with PEG. However, we found that some PEG derivatives, such as bis(3,5-dinitrobenzoyl)-poly(ethylene glycol) (PEG-DNB2) and bis(2,4-dinitrophenylamino)-poly(ethylene glycol) (PEG-DNP2), formed complexes with  $\gamma$ -CD to give crystalline compounds in high yields. On the other hand,  $\alpha$ -CD did not form complexes with these PEG derivatives, because the substituents at the end groups are too large to penetrate  $\alpha$ -CD cavities. By using PEG with fluorescent probe groups attached to the ends, we have been able to establish that these polyrotaxanes are composed of double chains of PEGs threaded through the  $\gamma$ -CDs (Harada et al., 1994b).



**Figure 14-30.** Proposed structure of the  $\alpha$ -CD-PEG complex.

We isolated the complexes of bis(1-naphthylacetyl)-PEG (PEG-1N2) and bis(2-naphthylacetyl)-PEG (PEG-2N2) with  $\gamma$ -CD using standard methods. NMR spectra indicate that the complexes have a PEG :  $\gamma$ -CD ratio of 4 : 1. The emission spectra of the  $\gamma$ -CD/PEG-2N2 complex show a large contribution from excimers, but only a small contribution from monomeric naphthyls. In contrast, the emission spectra of  $\alpha$ -CD/PEG-2N2 only show emission from monomeric naphthyls. These results indicate that  $\alpha$ -CD is threaded by a single PEG chain, whereas  $\gamma$ -CD is threaded by two. The spectra of PEG-1N2 with CDs showed the same results.

The diameter of the  $\gamma$ -CD cavity is 8.5–9 Å (0.85–0.9 nm), which is twice as large as that of  $\alpha$ -CD (4.5 Å). However, the depth of the cavity of  $\gamma$ -CD is the same as that of  $\alpha$ -CD and  $\beta$ -CD (7 Å), which corresponds to the length of two ethylene glycol units. Molecular model studies indicate that the  $\gamma$ -CD cavity is large enough to accommodate a double chain of PEG, whereas the  $\alpha$ -CD cavities are too small to do this.

#### 14.3.2.2 Poly(propylene glycol)

$\beta$ -CD does not form polyrotaxanes with PEG of any molecular weight. However,  $\beta$ -CD was found to form polyrotaxanes with poly(propylene glycol) (PPG), which has methyl groups on a PEG chain, to give crystalline compounds (Harada and Kamachi, 1990b; Harada et al., 1995a).  $\alpha$ -CD does not form polyrotaxanes with PPG of any molecular weight. An  $\alpha$ -CD cavity is too small for PPG to penetrate, due to steric hindrance by methyl groups on the main chain.  $\beta$ -CD did not form polyrotaxanes with the dimer and the trimer, but formed polyrotaxanes with PPG of molecular weight over 400. The yields increased with an increase in the molecular weight of PPG. The poly-

rotaxanes were obtained almost quantitatively with PPG of molecular weight of about 1000. However, the yields decreased with the increase in the molecular weight of PPG. This behavior is different from polyrotaxane formation between  $\alpha$ -CD and PEG. This may be due to the fact that PPG is more hydrophobic owing to the methyl group of the main chain.  $\gamma$ -CD also forms polyrotaxanes with PPG in high yields. The neighboring cyclodextrins bound on a polymer chain interact with each other by forming hydrogen bonds. This view is consistent with the fact that PPG does not form crystalline complexes with 2,6-di-*O*-methyl- $\beta$ -CD, 2,3,6-tri-*O*-methyl- $\beta$ -CD, and water-soluble  $\beta$ -CD polymer. These compounds are thought to be unable to form crystalline complexes, because they cannot form hydrogen bonds due to the lack of hydroxyl groups.

The stoichiometries are again 2 : 1 (two propylene units : CD). Molecular model studies show that PPG chains are able to penetrate  $\beta$ -CD cavities, while the PPG chain cannot pass through the  $\alpha$ -CD cavity owing to the hindrance of the methyl group on the main chain. These views are in accordance with our results that  $\beta$ -CD formed polyrotaxanes with PPG, but  $\alpha$ -CD did not form polyrotaxanes with PPG. Model studies indicate further that the single cavity accommodates two propylene glycol units.

The  $^1\text{H}$  NMR spectra of the complex show that the methyl peak of PPG is broader in the polyrotaxane, suggesting interactions between  $\beta$ -CD and the methyl group of PPG. The polyrotaxanes of  $\beta$ -CD with PPG of low molecular weight (MW = 400–700), which are isolated as crystalline polyrotaxanes, are soluble in a large amount of water. The polyrotaxanes are soluble in dimethyl sulfoxide and dimethylformamide. X-ray diffraction studies show that all of the polyrotaxanes are crystalline, in spite of the fact that PPG

is a liquid. X-ray patterns of the polyrotaxanes of PPG are similar to that of the complex between  $\beta$ -CD and *p*-nitroacetanilide, which was proven to have channel-type structures by single crystal X-ray studies.

#### 14.3.2.3 Poly(methyl vinyl ether)

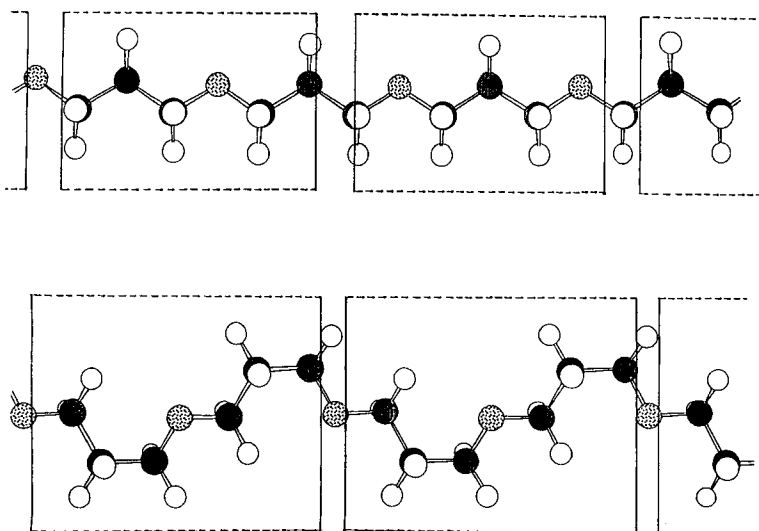
Poly(methyl vinyl ether), which has the same composition as PPG but methoxy groups as side chains, did not form polyrotaxanes with  $\alpha$ - and  $\beta$ -CDs. However, it formed polyrotaxanes with  $\gamma$ -CD (Harada et al. 1993 g). In this case, the stoichiometry is 3 : 1 (monomer units : CD). The number of atoms in the main chain included in a single CD is six, which is the same as for  $\alpha$ -CD-PEG polyrotaxanes and  $\beta$ -CD-PPG polyrotaxanes.

#### 14.3.2.4 Poly(oxytrimethylene)

$\alpha$ -CD formed complexes with poly(oxytrimethylene) (POx) to give crystalline polyrotaxanes in high yield, although it did not form polyrotaxanes with poly(propy-

lene glycol) (PPG) of any molecular weight, which has the same composition ( $C_3H_6O$ )<sub>n</sub> but with methyl groups as side chains, nor with poly(methyl vinyl ether) (PMeVE), which has the same composition but has methoxy groups as side chains (Harada et al., 1995 a). A POx chain is slim enough to penetrate an  $\alpha$ -CD cavity. The yields increased with the increase in the molecular weight of POx, reached a maximum at about a molecular weight of 1000, and then decreased. This result is different from that for polyrotaxane formation between  $\alpha$ -CD and PEG. This may be due to the fact that POx is more hydrophobic than PEG owing to the methylene group of the main chain.

$\beta$ -CD was also found to form polyrotaxanes with POx to give crystalline compounds. This result is in contrast to that for polyrotaxane formation between  $\beta$ -CD and PEG. This is due to the fact that POx is more hydrophobic than PEG, and/or to the fact that POx takes not only a planar zigzag conformation but also other conformations which need larger cavities to accommodate the chain. So the polyrotaxane between  $\beta$ -CD and POx can be stabilized. The yields



**Figure 14-31.** Proposed structures of complexes of POx with  $\alpha$ -CD (upper) and with  $\beta$ -CD (lower).

of the polyrotaxanes of  $\beta$ -CD are lower than those of  $\alpha$ -CD over the molecular weight range, indicating that the fitness of POx to  $\alpha$ -CD is better than that with  $\beta$ -CD (Fig. 14-31).

$\gamma$ -CD did not form polyrotaxanes with POx under the same conditions. The structural prerequisite for precipitation of the complex is that the polymer chain fixes well in a CD cavity and is hydrophobic enough to stabilize the complex.

#### 14.3.2.5 Poly(tetrahydrofuran)

Cyclodextrins were found to form polyrotaxanes with poly(tetrahydrofuran) (PTHF) of various molecular weights (Harada et al., 1995b). It is interesting that  $\gamma$ -CD formed polyrotaxanes with PTHF in high yields, although it did not form polyrotaxanes with poly(oxytrimethylene), which has a three instead of a four methylene unit of PTHF. The yield of the polyrotaxanes of  $\alpha$ -CD with PTHF decreased with increases in the molecular weight of PTHF. The yield of the polyrotaxanes of  $\gamma$ -CD with PTHF increased with increases in the molecular weight of the polymer, reached a maximum at a molecular weight of around 1000, and then decreased with further increases in the molecular weight. The stoichiometry of the polyrotaxane between  $\alpha$ -CD and PTHF is 1 : 1.5 (CD: monomer unit). The length of the guest polymer included in a single  $\alpha$ -CD cavity is consistent with that of a PEG rotaxane. These polyrotaxanes were found to assume channel-type structures by X-ray studies and solid state NMR studies.

#### 14.3.2.6 Oligoethylene

We found that cyclodextrins form complexes not only with hydrophilic polymers but also with hydrophobic polymers, such

as oligoethylene and polyisobutylene.  $\alpha$ -CD forms polyrotaxanes with oligoethylene (OE), although  $\beta$ - and  $\gamma$ -CD did not form polyrotaxanes oligoethylenes under the same conditions.

When the aqueous solution of  $\alpha$ -CD with oligoethylene (OE) was heated to above the melting temperature of OE, followed by sonication, the solutions became turbid and the polyrotaxanes were formed as crystalline precipitates. OE was also found to form polyrotaxanes with  $\alpha$ -CD from dimethylformamide solutions of  $\alpha$ -CD to give stoichiometric compounds in a crystalline state in high yields. The yields of the polyrotaxanes of  $\alpha$ -CD were independent of the degree of polymerization when the polyrotaxanes were formed in aqueous media. The yields increase with increases in the  $n$  of OEs, and show a maximum at  $n=12$ . Then the yields decrease with increases in the  $n$  of OEs.

The  $\alpha$ -CD-OE polyrotaxanes could not be dissolved in water at all, even with heating. They are also insoluble in most organic solvents, except for dimethylformamide.

The stoichiometries of the polyrotaxanes were found to be 3 : 1 (ethylene unit :  $\alpha$ -CD), as measured by quantitative studies on the polyrotaxane formation and the  $^1\text{H}$  NMR spectra of the isolated polyrotaxanes.

$^{13}\text{C}$  CPMAS NMR and PST MAS NMR spectra of OE and polyrotaxanes show that the ethylene backbone in the polyrotaxanes is much more flexible than that in the uncomplexed state. The intensity ratios of the peaks of the ethylene backbone to those of  $\alpha$ -CD in the PST spectrum are higher than in the CP spectrum, indicating that, in the complex, the ethylene backbone is not as rigid as  $\alpha$ -CD is. These results are consistent with the views that the  $\alpha$ -CDs form a channel, which constructs the crystal frame of the complex, and the OE chain is included in the channel.

#### 14.3.2.7 Polyisobutylene

When polyisobutylene (PIB) was added to aqueous solutions of  $\gamma$ -CD and the mixture was sonicated at room temperature, the mixture became turbid and the polyrotaxanes were formed as crystalline precipitates (Harada et al., 1993 d).

$\alpha$ -CD did not form polyrotaxanes with PIB of any molecular weight.  $\beta$ -CD and  $\gamma$ -CD formed polyrotaxanes with PIB. However, the yields of the polyrotaxanes with  $\beta$ -CD decreased with increases in the molecular weight of PIB. In contrast, the yields of the polyrotaxanes with  $\gamma$ -CD increased with increases in the molecular weight, and the polyrotaxanes were obtained almost quantitatively with PIB of molecular weight 1000. The chain length selectivity is totally reversed between  $\beta$ -CD and  $\gamma$ -CD. In particular,  $\beta$ -CD formed complexes with the low molecular weight analogs, monomer and dimer. However,  $\gamma$ -CD did not form complexes with these low molecular weight compounds.

The stoichiometry is 3:1 (monomer unit : CD), suggesting that three isobutylene units were bound in each  $\gamma$ -CD cavity. The length of the three isobutylene units corresponds to the depth of the  $\gamma$ -CD.

The polyrotaxanes are crystalline and insoluble in water, even in boiling water. However, the addition of urea to the suspension of the complex on heating resulted in solubilization of the complex, indicating that hydrogen bonding between CDs plays an important role in stabilizing the complex. The X-ray diffraction pattern of the complex between  $\gamma$ -CD and PIB shows that the polyrotaxanes are crystalline and that the pattern of the polyrotaxane is totally different from that of nonincluded  $\gamma$ -CD but is similar to that of the polyrotaxane, which has been proven to have an extended column structure. Molecular model studies show that a

PIB chain is able to penetrate the  $\gamma$ -CD cavity, while the PIB chain cannot pass through the  $\alpha$ -CD cavity owing to the hindrance of the dimethyl groups on the main chain. Hindrance of the dimethyl groups makes it difficult for the PIB chain to penetrate  $\beta$ -CD cavities. These views are in accordance with the results that  $\gamma$ -CD formed a polyrotaxane with PIB but  $\alpha$ -CD did not form polyrotaxanes with PIB. Model studies further indicate that the single cavity accommodates three isobutylene units.

#### 14.3.2.8 Polyesters

Recently, Harada and co-workers found that some polyesters form inclusion complexes with cyclodextrins. Poly( $\epsilon$ -caprolacton) formed stoichiometric inclusion complexes with  $\alpha$ -cyclodextrin in high yields to give crystalline compounds (Harada et al., 1997 a). Poly(alkylene adipates) formed complexes with  $\alpha$ -cyclodextrin and  $\gamma$ -cyclodextrin in high yields (Harada et al., 1997 b).

#### 14.3.2.9 Molecular Necklace

We have prepared compounds in which many cyclodextrins are threaded on a single PEG chain and are trapped by capping the chain ends with bulky groups, as shown in Scheme 14-1 (Harada et al., 1992; Harada et al., 1993 c). This is the first example where many rings are imprisoned in a single molecule. We named this molecule a "molecular necklace". Wenz and co-workers also reported a rotaxane and a polyrotaxane of poly(iminooligomethylene) with many  $\alpha$ -CDs (Wenz and Keller, 1992; Wenz, 1994; Meier et al., 1996) (Fig. 14-32).

The inclusion complexes of  $\alpha$ -CD with PEG-bisamine (PEG-BA) were prepared by adding an aqueous solution of PEG-BA to a



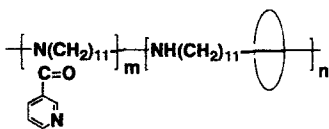
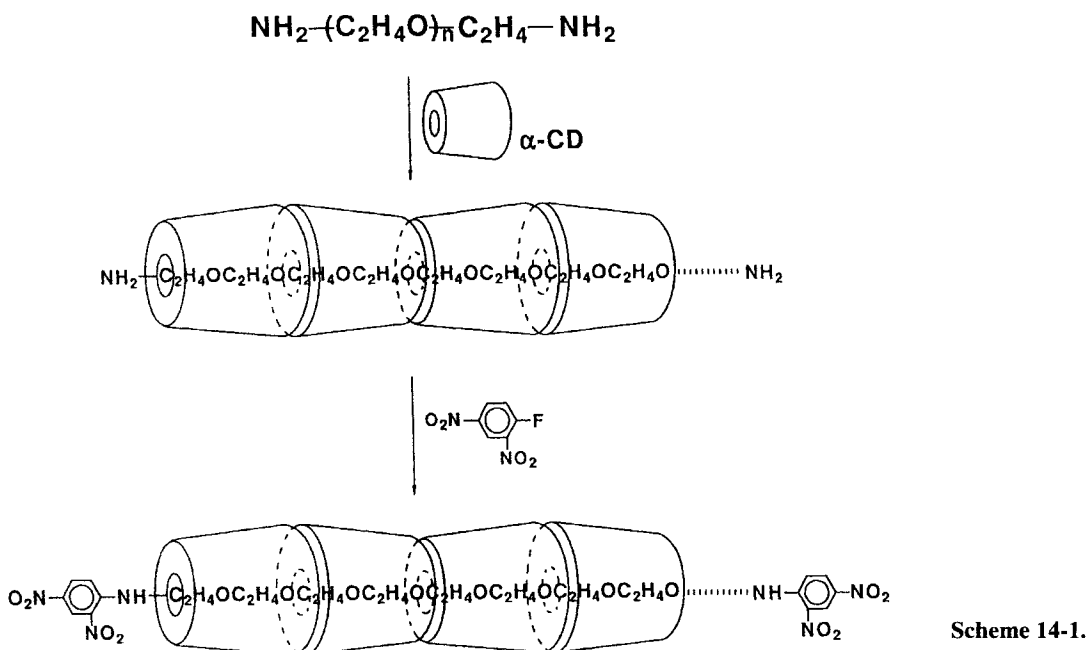


Figure 14-32. Polyrotaxanes containing polyamines.

saturated aqueous solution of  $\alpha$ -CD at room temperature, using a method similar to that used to prepare complexes of  $\alpha$ -CD and PEG. The resulting complex was allowed to react with an excess of 2,4-dinitrofluorobenzene, which is bulky enough to prevent dethreading. The product was purified by column chromatography on Sephadex G-50 by using dimethylsulfoxide (DMSO) as the solvent.

The products are insoluble in water and dimethylformamide, but they are soluble in DMSO and 0.1 N NaOH. The products were characterized by UV-vis, X-ray diffraction,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{13}\text{C}$  CP/MAS NMR, and 2D NOESY NMR spectra. 2D NOESY NMR spectra show that the signals of H-3

and H-5 protons of  $\alpha$ -CD, which are directed toward the inside of the cavity, correlate with the resonance of the  $\text{CH}_2$  of PEG, but the H-1, H-2, and H-4 protons, which are located outside the cavity, do not correlate with PEG. These results indicate that a PEG chain is included in  $\alpha$ -CD cavities.

Table 14-1 shows the results of the preparation of polyrotaxanes of various molecular weights. The number of CDs increases with an increase in the molecular weight. MN-3350, which was prepared from PEG (MW=3350), has 20–23 CDs on a PEG chain. This corresponds to a molar ratio of ethylene glycol units to  $\alpha$ -CDs of 3.9. More than half of the polymer chain is covered with  $\alpha$ -CDs. MN-1450 has 15  $\alpha$ -CDs on a PEG chain. The molar ratio of ethylene glycol units to  $\alpha$ -CD is 2.2. This ratio indicates that the molar ratio is almost stoichiometric; that is, the CDs are almost close packed from end-to-end of the polymer chain.

In these cases, the polymers used are polydisperse and the number of CDs in the

**Table 14-1.** Polyrotaxanes prepared from PEG-BA with various molecular weights.

Polyrotaxane	Molecular weight <sup>b</sup>	Number of ethylene glycol units (included + nonincluded)	Number of threaded $\alpha$ -CD <sup>b</sup>	Molar ratio of ethylene glycol units to $\alpha$ -CD
MN-1450	16 500	33 (33 + 0)	15	2.2
MN-2000	20 000	45 (36 + 9)	18	2.5
MN*-2001 <sup>a</sup>	19 000	45 (34 + 11)	17	2.6
MN-3350	23 500	77 (40 + 37)	20	3.9
MN-8500	44 000	193 (72 + 121)	36	5.4
MN-20 000	89 000	454 (140 + 314)	70	6.5

<sup>a</sup> Prepared from Jeffamine ED-2001; <sup>b</sup> Calculated from UV-vis spectra, optical rotation, and <sup>1</sup>H NMR spectra.

polymer chain is also polydisperse. Therefore, the rotaxanes obtained are highly heterogeneous. In order to obtain homogeneous polyrotaxanes, we have prepared monodisperse PEGs (28mer, MW = 1248), because PEGs of molecular weight 1000–1500 were found to be most favorable for complex formation. We have succeeded in preparing complexes between  $\alpha$ -CDs and monodisperse diamino-PEG, and in imprisoning 12  $\alpha$ -CDs on monodisperse diamino-PEG by capping PEG chain ends with bulky substituents (Harada et al., 1993 e).

The bulky end groups (dinitrophenyl groups) were removed by cleaving the C-N bond with a strong base, and the CDs were recovered. The number of cyclodextrins in the polyrotaxane can be estimated from the <sup>1</sup>H NMR spectra, optical rotation, and UV-vis spectra. Twelve  $\alpha$ -CDs were found to be included in the polyrotaxane.

#### 14.3.2.10 Inclusion Polymerization

Ogata et al. (1979) prepared inclusion complexes of various diamine (hexamethylene diamine, *p*-xylylenediamine, *m*-xylylenediamine) complexes of  $\beta$ -CD. Polyamides were obtained by the condensation

of dibasic acid chlorides and the inclusion complexes of the diamine. The IR spectra of the complexes showed absorption bands characteristic of amides and cyclodextrins. The complexes were also characterized by elemental analyses. The solubilities of the polyrotaxanes were different from those of the standard polyamides. The viscosities of the products were low, indicating that the molecular weights were low. The details have not been reported.

Maciejewski (1979) reported the radiation polymerization and copolymerization of vinylidene chlorides as adducts with  $\beta$ -CD. The molecular weight of the product was about 20 000 and the product contained 80% cyclodextrin. This corresponds to 1 : 2.9 complexation, that is, a single macrocycle to 2.9 units of vinylidene chloride. Although there is a possibility of chain transfer reactions in the radiation polymerization of  $\beta$ -CD with vinyl monomers, polyrotaxanes might be formed, because polymerization of the crystalline adduct of  $\beta$ -CD with methyl methacrylate did not produce a stable polymer. The instability of the complexes formed from methyl methacrylate or styrene and  $\beta$ -CD may be explained by the possibility that the monomers are arranged in the  $\beta$ -CD cavity in such a way that the

double bonds protrude from the cavity. As a result of polymerization of the complexes,  $\beta$ -CD is not threaded but only complexes to pendant substituents and easily de-threads from the complex during purification.

Maciejewski et al. (1979) carried out the polymerization of methyl methacrylate, styrene, and methacrylonitrile in the presence of  $\beta$ -CD, or as their complexes using azobisisobutyronitrile as an initiator.

When methyl acrylate, methacrylonitrile, or styrene was polymerized in the presence of  $\beta$ -CD, CD was not threaded, and the corresponding homopolymers were isolated. However, when vinylidene chloride was used as a monomer in the presence of  $\beta$ -CD in dimethylformamide, the complexes with various amounts of CD were obtained. With increasing temperature, the ratio of polyrotaxane to homopolymer increased: the content of CD is maximized at about 100 °C. The product was soluble in dimethylformamide and insoluble in other organic solvents. Polyrotaxane-type structures were proposed.

### 14.3.3 Cyclophanes

Lipatova et al. (1985) used a cyclic urethane as the ring component during the polymerization of styrene. An X-ray scattering study of the polymer suggested that one cyclic urethane is incorporated every 18–19 monomer units along the backbone, while the  $\text{ZnCl}_2$  complex produced a polymer where one cyclic urethane is incorporated every 6–7 monomer units.

Harrison (1977) showed that polymer chains could be threaded by cyclic alkanes by means of gas chromatography. From gas chromatographic results on Carbowax for a series of cycloalkanes and the linear alkanes, he reported that C26 and larger rings

can thread polymer chains of the stationary phase. The linear and smaller rings behaved normally. He thought that when a large macrocycle passed through the column the macrocycles threaded onto the polymer chain and the vapor pressure decreased, which resulted in a delay in elution.

## 14.4 Side Chain Polyrotaxanes

Side chain polyrotaxanes containing ring molecules in the side chain of a polymer chain have been prepared by Ritter and co-worker (Born and Ritter, 1991). Recently, they prepared side chain polyrotaxanes with a tandem structure based on cyclodextrins and a polymethacrylate main chain (Born and Ritter, 1995). More recently, they obtained topologically unique side chain polyrotaxanes based on triacetyl- $\alpha$ -CD and a poly(ether sulfone) main chain, in which cyclodextrins are arranged uniformly, as shown in Fig. 14-33 (Born and Ritter, 1996).

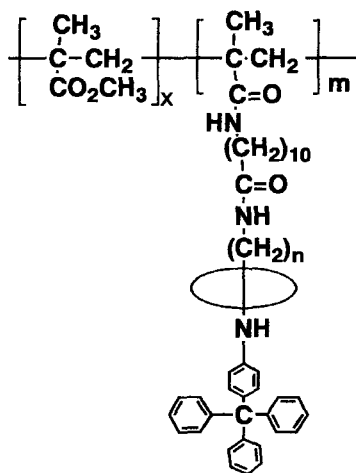


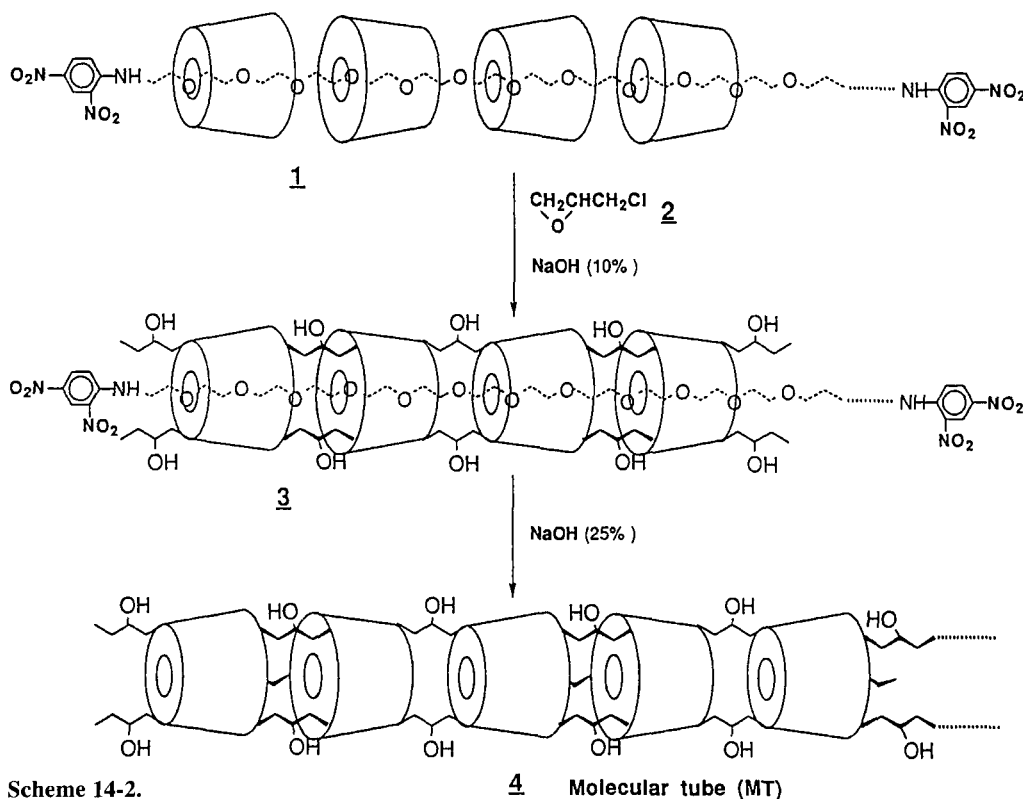
Figure 14-33. Side chain polyrotaxane.

## 14.5 Preparation of Tubular Polymers from Polyrotaxanes

Tubular polymers have been prepared from polyrotaxanes, as shown in Scheme 14-2 (Harada et al., 1993f, 1995c). Polyrotaxanes were prepared as described above. In this case, poly(ethylene glycol) of molecular weight 1450 was used, because  $\alpha$ -CD forms complexes with PEG of molecular weight 600–2000 most efficiently. The complexes are nearly stoichiometric (two ethylene glycol units: a single cyclodextrin molecule), that is,  $\alpha$ -CDs are almost closed packed from end to end of the polymer chain. The polyrotaxane was dissolved in 10% NaOH solution, and epichlorohydrin was added to the solution. The crosslinked polyrotaxanes were isolated and treated with a strong base (25% NaOH) with heat-

ing to remove bulky stoppers. The product was purified by column chromatography on Sephadex. Two peaks were observed: the one at the void volume, which is detected only by optical rotation, is identified as the product, the molecular tube. The second peak, which was only detected by UV (360 nm), is assigned as a dinitrophenyl group (DNP). The molecular weight of the molecular tube was estimated by GPC on Sephadex G-100, using dextran as the standard, to be about 17 000. The yield of the final product is 92%.

The product was soluble in water, DMF, and dimethylsulfoxide (DMSO), although polyrotaxanes are insoluble in water and DMF and soluble in DMSO. The product was characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR, and UV spectra and GPC. The  $^1\text{H}$  NMR spectra of the molecular tube in  $\text{D}_2\text{O}$  and in



Scheme 14-2.

4 Molecular tube (MT)

DMSO- $d_6$ , and the  $^{13}\text{C}$  NMR spectra show that both CD and the bridge can be observed. All the peaks of the  $^1\text{H}$  NMR spectrum are broadened, indicating that the product is polymeric.

When the solution of the molecular tube was added to a KI- $\text{I}_2$  solution (pale yellow), the solution turned deep red instantaneously, although the addition of an  $\alpha$ -CD solution to KI- $\text{I}_2$  solution caused nothing to happen. On the addition of randomly cross-linked  $\alpha$ -CD, no visible changes took place. The change in the spectra was found to be at a maximum at one to one (cyclodextrin unit and  $\text{I}_3^-$ ).

## 14.6 Summary

Recently, many kinds of polyrotaxane have been prepared and characterized by combinations of polymer chains, ring molecules, and stoppers. Novel properties have been found in polyrotaxanes compared to mixtures of the components.

Crown ethers, cyclophanes, and cyclodextrin have been found to be able to be used for ring components for the synthesis of polyrotaxanes. Crown ethers have been found to be threaded onto a polymer chain as a statistical way to form polyrotaxanes. Cyclodextrins have been found to form inclusion complexes, not only with low molecular weight compounds, but also with hydrophilic polymers and hydrophobic polymers, to give stoichiometric compounds in high yields. The selectivities shown by cyclodextrins toward polymers are much higher than for low molecular weight compounds. This is due to the fact that the guest polymers have a lot of recognition sites. Polyrotaxanes in which many CDs are entrapped on a polymer chain have been prepared. This is one of the first examples that many ring molecules are threaded on a poly-

mer chain. Tubular polymers were prepared from the polyrotaxanes. Such molecular tubes have potential uses for ion channels, catalysts, capsules, and separation devices. Reactions in organized assemblies give highly ordered structures. This kind of complex formation can be utilized to create new supramolecular architectures and functions.

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## 15 Polymerization in Organized Media

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## List of Symbols and Abbreviations

$a, b, c$	coordinates
$A$	pre-exponential factor
$d$	layer spacing
$d_2$	distance
$E_a$	activation energy
$h$	Planck's constant
$k$	rate of polymerization
$n$	director
$q_0$	helix pitch
$R$	gas constant
$R_p$	polymerization rate
$S_1$	distance
$T$	temperature
$x, y$	number
$x, y, z$	dimensions
$\gamma$	angle
$\nu$	frequency
$\pi$	surface pressure
$\sigma_e$	mechanical field
DNA	deoxyribonucleic acid
DP	degree of polymerization
LB	Langmuir–Blodgett
LCP	liquid-crystalline polymer
Me	methyl
NMR	nuclear magnetic resonance
PMMA	poly(methylmethacrylate)
RNA	ribonucleic acid
SAM	self-assembling monolayer
UV	ultraviolet

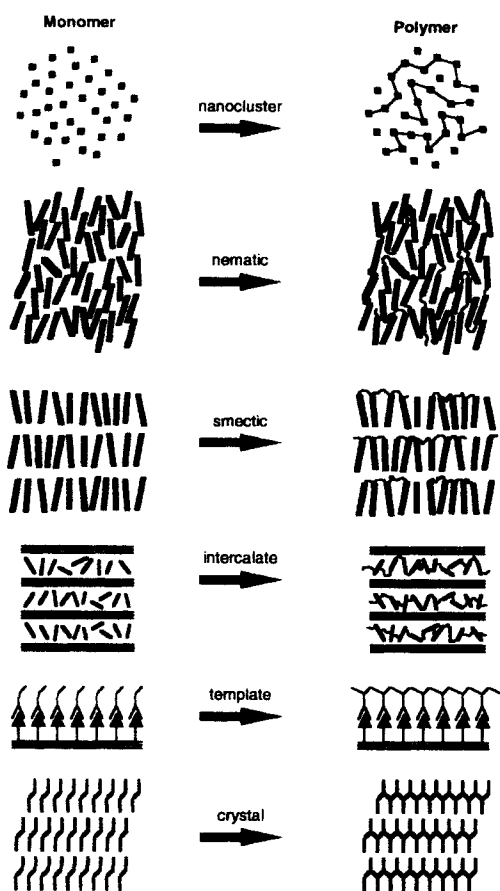
## 15.1 Introduction

In the 1920s, Carothers defined polymers as molecules containing repeating structural units which are incapable of independent existence (Carothers, 1928; Mark and Whitby, 1940). It is well known that these *carothersian* polymers and their enormous monomeric alphabets can generate many useful materials by polymerization in bulk or solution. The covalent connections among monomers take place commonly in the isotropic media of neat liquids, solutions, melts, or gaseous phases. Therefore the structure of growing macromolecules in isotropic media is controlled mainly by the local chemistry near the chain ends. The nature of functional groups or high energy moieties at the ends of chains controls stereochemistry, regiochemistry, and the chemical sequence when more than one monomer can add to the growing macromolecule. The viscosity and chemistry of the highly entropic medium determines the polymerization kinetics and the average molar mass of the product. However, the physical structure of this medium plays only a minor role in defining the covalent architecture and the final degree of order in the product. If the medium in which polymerization is taking place were to have a significant order parameter, then in principle the medium could deeply affect the resulting macromolecular architecture and final three-dimensional organization. This idea has been the dream driving research in the area of polymerization in organized media over the past few decades. However, it is not clear at the moment whether the most important discoveries in this field have been made.

The order parameter of an organized polymerization medium could vary over a fairly wide range, Fig. 15-1 shows examples of such media. At one extreme, polymerization could occur in the localized and dynam-

ic environment of anisotropic molecular clusters. At the opposite extreme, the polymerization may be topochemical in nature occurring in the positionally static environment of a crystal. The intermediate possibilities would be polymerization in mesophases possessing order parameters of liquid crystals. Here the medium might be orientationally ordered as in nematic phases, and in some cases helically twisted as well (cholesterics). In other cases monomers might be organized in layers, offering the possibility of polymerization in two-dimensional confinement. Alternatively, two-dimensional environments for polymerization can be created artificially at interfaces or solid surfaces. Other fascinating possibilities would mimic biological processes, such as the replication of DNA, its transcription into RNA, and the subsequent translation into proteins. All these reactions could be considered polymerizations in the organized medium of a one-dimensional template. In the context of templating polymerizations, there have been previous reports with synthetic systems in which a polymer template is used to influence the tacticity of the growing polymer (Yau and Stupp, 1985; Butler et al., 1973 a, b, c, d). However, the implementation of such templating polymerizations in synthetic systems may emerge in the future with features that more closely resemble biological specificity.

One reason to be interested in the field of polymerization in organized media is certainly the potential of molecularly designed materials. Decades to come may utilize molecular materials of polymeric nature with several properties integrated in a single structure. To be of high value, these materials will probably have to be self-organizing in nature and not require complex hardware to produce. In this context, polymerization proceeding in an organized medium, which is preserved after conversion of the system



**Figure 15-1.** A schematic illustration of polymerization in various ordered states.

to a polymeric substance, may find many important technological applications. One important use may be in the repair of humans with biomaterials. In such systems, monomers may be delivered in a pre-organized fashion to human tissues for a specific set of functions and then polymerized *in situ* with little external energy. Generally speaking, all technological applications in which require molecular materials with high degrees of order over macroscopic distances are likely to benefit from polymerization in organized media, for example, waveguides, nonlinear optical films, anisotropic electrical conductors, highly selective mem-

branes, sensors, and many others. This chapter reviews some of the work carried out recently on polymerization in organized media. The objective has been to give the reader some idea of the facts found thus far, and help those interested to decide what major knowledge gaps and challenges have been missed in this area. An exhaustive review and list of references is very difficult these days and so we apologize to readers for any omissions in our review of the literature.

Well-established topics explored in this article include topochemical polymerizations, polymerization in thermotropic and lyotropic liquid crystals, the use of vesicles and bilayers as media for polymerization, polymerization in Langmuir–Blodgett films, and intercalated systems. Topochemical polymerizations have been found to be exquisitely sensitive to molecular packing in the solid state, often leading to highly strained solids after reaction as a result of dimensional changes. Analogous reactions in the liquid crystalline rather than the crystalline state have enormous potential to yield functional solids and also to deliver polymers of unusual architecture and shape persistence. With the characteristic mobility of molecules in the liquid-crystalline state, these polymerizations offer the possibility of confining reactions in spaces of low dimensionality, creating potentially interesting macromolecular architectures. This area is under development and important discoveries will be made in the future. We have also included some discussion on the thermodynamics and kinetics of polymerization in ordered media. The article ends with two sections on less established topics, namely, the formation of two-dimensional polymers in ordered media and the future prospects for the polymerization of ordered supramolecular units to create nanostructures.

## 15.2 Topochemical Systems

Topochemical solid state reactions are facilitated by the regular arrangement of the precursor molecules in a manner conducive to their interaction. The reaction of these molecules is typically initiated by irradiation of the lattice, which gives rise to an excited state. The key to topochemical reactions is the ability of these excited state molecules to react with little or no atomic displacement. Reaction occurs simply with the shift of electron density and a change in the bonding pattern of the atoms. Known reactions include the dimerization of crystallized molecules or the coupling of two molecules that have been cocrystallized (Cohen and Schmidt, 1964; Schmidt, 1971). Interesting topochemical polymerizations which link monomers into linear macromolecules have been discovered over the past few decades, and the classical example is that of diacetylenes reported by Wegner (1969, 1971, 1977). Polymers can be synthesized by the reaction of molecules with suitable polymerizable units in the crystalline state, as well as in media of lower order, such as liquid crystals. Topochemical polymerizations are ideal examples of reactions defined as macromolecular synthesis in organized media. Beyond scientific curiosity, topochemical polymerization offers unique control over the stereoregularity, crystallinity, and molecular weight of the resulting polymers. Especially in polymers with conjugated backbones, this control has proven difficult to realize through conventional polymerization and processing techniques (Mat-

sumoto et al., 1996; Enkelmann, 1984). As a result, topochemical polymerizations are of interest in the fabrication of polymer devices that require this level of structural control.

Topochemical polymerizations typically proceed to very high degrees of conversion, often limited only by the grain boundaries or other defects in the monomeric lattice. Monomer systems based on diacetylenes (Likhatchev et al., 1995; Wegner, 1971; Kuhling et al., 1990; Mayerle et al., 1979; Okuno et al., 1992), dienes (Matsumoto et al., 1996; Tieke, 1985), and various other diolefinic moieties (Maekawa et al., 1991; Peachey and Eckhardt, 1993) have been reported to undergo topochemical polymerization. Polymerizations of substituted diacetylenes are the most common type of topochemical reaction. A number of general structural guidelines can be given for the required molecular packing that is conducive to topochemical polymerizations. Structural studies of various crystals and their corresponding reactivity have provided a range of interatomic spacings and orientations. Figure 15-2 shows a schematic diagram of diacetylene packing, before and after polymerization. The "topochemical principle" predicts reactivity in cases where  $d_2$  is in the range of 0.47–0.52 nm,  $s_1$  is less than 0.4 nm, and  $\gamma_1$  is about  $45^\circ$  (Wegner, 1977; Enkelmann, 1984; Baughman and Melveger, 1973; Cao and Mallouk, 1991; Zutout et al., 1992; Yan et al., 1992). This packing allows the 1,4 addition polymerization of neighboring diacetylenes to occur with a minimum of molecular dis-

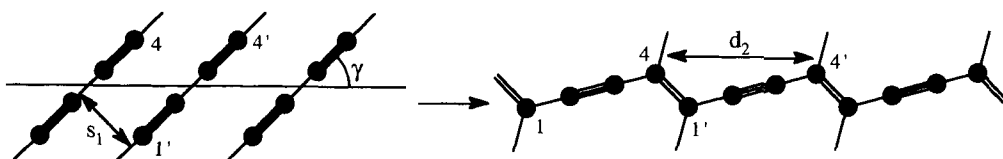
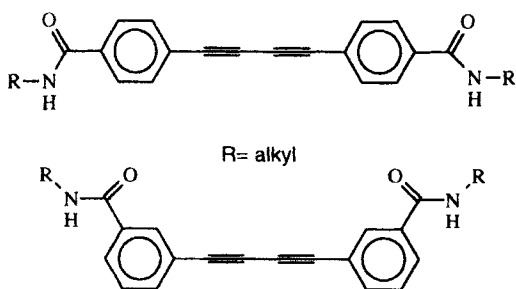


Figure 15-2. Geometrical constraints in the topochemical polymerization of diacetylenes.



**Figure 15-3.** Substituted butadiynylene dibenzamides (Likhatchev et al., 1995).

placement. Obviously, since the polymerization is sensitive to molecular packing, the degree of conversion is highly dependent on how well the packing of the monomer fits that of the polymer (Enkelman, 1984; Li and Stupp, 1997; Gresham et al., 1998).

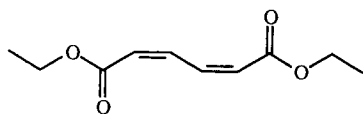
Ideal homogeneous topochemical polymerizations occur in systems for which the growing polymer and monomer crystal structures are isomorphous; although small changes are observed in the lattice parameters with conversion, the system can always be described by a solid solution of the polymer and monomer. Baughman and co-workers describe the conversion kinetics in these systems via crystal strain theory, which describes the autoacceleration effects seen in many such systems. Here conversion is seen to increase dramatically after some induction period (Baughman and Melveger, 1973; Baughman 1978; Baughman and Chance, 1980). Many diacetylene systems show moderate reactivity and limited overall conversion; their behavior can be rationalized by the mismatch in the polymer and monomer crystalline lattices. At low conversion, the system resides as a solid solution of polymer within the monomer lattice. As conversion passes some transition point, the system can be described more accurately as a solid solution of monomer on the polymer lattice; conversion rates typically

increase, since the barrier to polymerization is lower on the polymer lattice. Further mismatch in the polymer and monomer lattices causes heterogeneous polymerization, in which a phase-separated polymer phase is nucleated (typically at a crystal edge or defect) (Enkelmann, 1984).

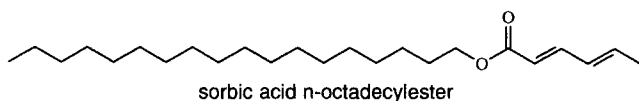
The structural requirements for topochemical polymerizations outlined above neglect a number of factors. The ability of a diacetylene monomer to readily polymerize to full conversion is related to the flexibility in monomer packing. If a certain amount of atomic displacement can be accommodated without the disruption of overall packing, small changes in the lattice parameters between the polymer and monomer are less likely to cause phase separation. If, however, the system is especially rigid (e.g., due to a network of hydrogen bonds), little tolerance is observed for the structural requirements outlined above (Wegner, 1971; Kuhling et al., 1990; Mayerle et al., 1979; Wilbenga, 1940). This was dramatically observed in systems of ortho-, meta-, and para-substituted butadiynylene dibenzamides (see Fig. 15-3). In general, it has been found that aromatic diacetylenes with hydrogen bonding substituents in the ortho and meta positions typically undergo topochemical polymerization, while the para-substituted ones do not, presumably due to the stiff hydrogen bonding in the later (Likhatcher et al., 1995; Wegner, 1971). However, para-substituted butadiynylene dibenzamides were polymerizable if the alkyl chains were long enough to dominate packing, limiting the formation of hydrogen bonds between the amides (Likhatcher et al., 1995; Salcedo et al., 1996). Related to this topic, some diacetylene polymerizations are known to occur in liquid-crystalline phases, but not in the corresponding crystalline state, possibly due to the greater spatial degrees of freedom allowed in liquid crystals (this will be dis-

cussed further in the section on polymerization in thermotropic liquid-crystalline systems) (Okuno et al., 1992; Son, 1994).

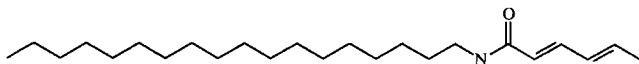
Diacetylene monomers are not the only molecules known to undergo topochemical polymerization. There are a number of butadiene derivatives with structures analogous to those of diacetylenes which are also able to undergo 1,4 addition polymerization, if molecular packing permits. Matsumoto et al. (1996) studied the polymerization of dialkyl muconates of various stereochemistries (Fig. 15-4). Among the molecules investigated in this series, it was found that only (*cis,cis*) diethyl (*E,E*)-2,4-dihexadienoate was able to undergo topochemical polymerization. Apparently, the packing of other stereoisomers is not conducive to their solid state polymerization (despite their ability to polymerize in solution with the appropriate initiators). This demonstrates how subtle packing effects can be in topochemical polymerizations. In fact, muconates with substitutions other than ethyl showed no tendency to polymerize in the solid state. Interestingly, the solid state polymerization of the *cis,cis*-ethyl derivative resulted in an ultrahigh molecular weight product ( $10^7$  daltons) with a highly



**Figure 15-4.** Diethyl *cis,cis*-2,4-dihexadienoate (Matsumoto et al., 1996).



sorbic acid n-octadecylester



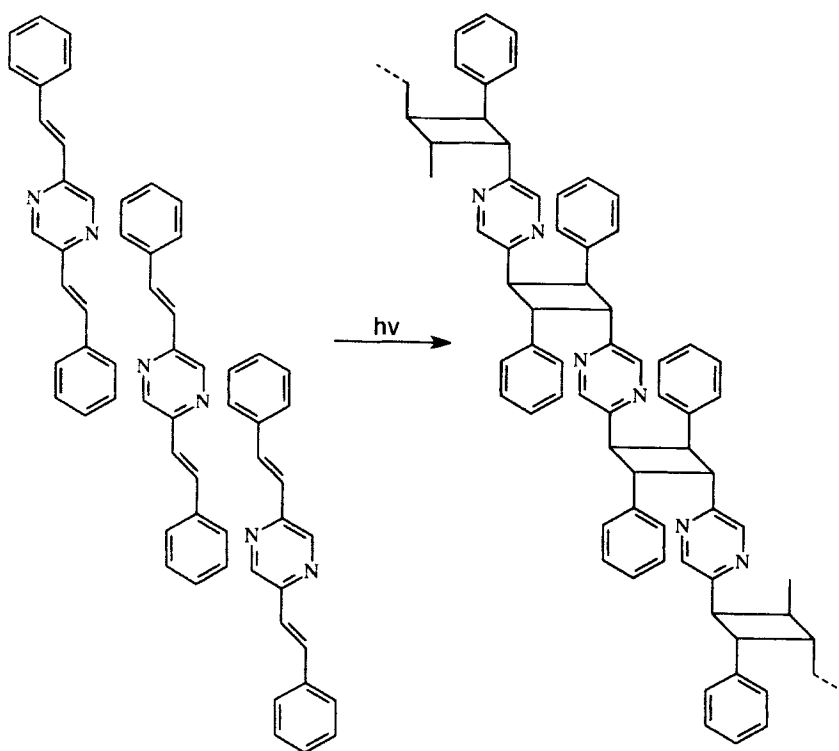
sorbic acid n-octadecylamide

stereoregular structure (Matsumoto et al., 1996; Tieke, 1985). Similarly, long chain alkylester and alkylamide derivatives of sorbic acid also exhibit topochemical reactivity, specifically undergoing 1,4 addition polymerization (see Fig. 15-5). Packing in these systems is governed by the side chains, which control the distance between the reactive groups and inhibit 2+2 dimerization (Tieke, 1985). Conversely, 2+2 dimerizations have been exploited in the design of topochemically polymerizable monomers. Molecules based on distyrylpyperazine, bispyridylvinyl benzene, and other similar molecules have two reactive olefinic bonds and often pack favorably for the formation of polymeric materials (see Fig. 15-6) (Maekawa et al., 1991; Peachey and Eckhardt, 1993).

### 15.3 Thermotropic Systems

Thermotropic liquid crystals offer many systems for the study of polymerization in organized media, combining, at least in principle, their characteristic order parameters with molecular mobility in a solventless environment. Typically, systems are based on a combination of a mesogenic and a monomeric unit, either as a discrete molecule or as a crosslinkable, side chain liquid crystalline polymer (Chein and Coda, 1994; Percec and Zheng, 1992 a, b; Symons et al., 1993). Functionalities include polymerizable units such as acetylene (Okuno et al.,

**Figure 15-5.** Sorbic acids derivatives (Tieke, 1985).

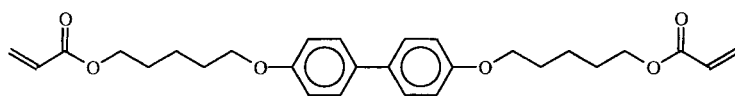


**Figure 15-6.** 2+2 photopolymerization of distyrylpyperazine (Wegner, 1977).

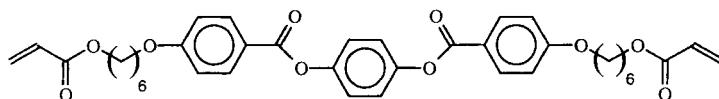
1992; Son, 1994; Cambell et al., 1993; Douglas et al., 1994), vinyl (Hikmet et al., 1993), acrylates (Qian and Litt, 1992; Broer et al., 1991; Kitzerow et al., 1993; Hikmet et al., 1995; Favre-Nicolin and Lub, 1996; Trollsas et al., 1996 a), epoxide (Barday et al., 1992) etc. The polymerizable mesogenic moieties organize in various thermodynamically stable phases with order between that of the crystalline and isotropic states. Some of these systems will require other components, such as crosslinking agents, initiators, or catalysts, and the challenge faced is that such additives may destabilize the mesophase or reduce its order parameter. Methods and conditions of initiation vary and include photoinitiation and thermal initiation both with and without added initiator molecules (Qian and Litt, 1992; Broer et al., 1991; Chain and Cada,

1991; Hikmet et al., 1993; Favre-Nicolin and Lub, 1996; Hikmet and Lub, 1995).

As briefly discussed in the last section, there are a number of instances of topochemical polymerizations carried out in thermotropic liquid crystals. Diacetylene monomers that undergo topochemical polymerization in the solid state often possess mesogenic groups which aid the alignment of the diacetylenes (Enkelmann, 1984). As a result, some show a variety of liquid-crystalline phases when heated above the crystal melting temperature (Okuno et al., 1992; Cambell et al. 1993; Schen et al., 1991). Smectic phases, especially those of higher order, have shown packing conducive to topochemical polymerization (Okuno et al., 1992). In general, polymerization in the liquid-crystalline state suffers from the same problems of misalignment as in the



**X:** 4,4'-bis-[5-(acryloyloxy)pentyloxy]biphenyl



**Y:** 1,4-phenylene bis[4-(6-acryloyloxyhexyloxy)benzoate]

**Figure 15-7.** Polymerizable thermotropic liquid crystalline acrylates: **X** (Qian and Litt, 1992), **Y** (Broer et al., 1991).

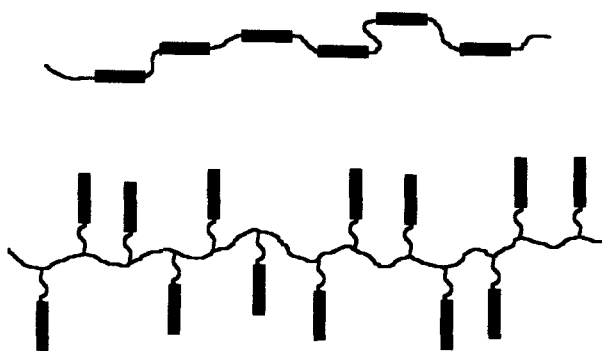
crystal case. That is, deviations in the packing of the monomer and polymer components can cause phase separation, accompanied by low degrees of polymerization. However, since liquid crystal systems are typically more tolerant of molecular motion and packing distortions, these systems are less sensitive than their crystalline counterparts. In fact, cases exist in which topochemical polymerization was not observed in the crystalline system because of specific packing restrictions; however, reactivity was seen in the liquid-crystalline state (Okuno et al., 1992).

The effect of ordering on the reactivity of the polymerizable groups is complex and depends on the nature of the phase, the molecular structure of the mesogen, and type of polymerizable moiety. In many instances, especially in the case of smectic phases, polymerization is enhanced by a 'topochemical effect' due to the alignment of the polymerizable groups. The proximity of the polymerizable groups allows for their reaction with minimal diffusion, leading to high conversion and facile kinetics (Qian and Litt, 1992; Okuno et al., 1992). However, in phases of lower order (nematic), where there is less registration between the polymerizable groups, the effect of order is unpredictable. Some systems show enhanced rates of reaction (Douglas et al.,

1994), while in others order seems to hinder diffusion, limiting the overall conversion and rate of polymerization (Spencer and Berry, 1992). A number of good examples are offered by polymerization of mesogenic diacrylate monomers (see Fig. 15-7). Qian and Litt (1992) found the photopolymerization of diacrylate monomer (**X**) in the smectic E phase resulted in nearly 100% conversion of the polymerizable groups. Since the polymerization caused only small changes in the unit cell, the order of the phase was preserved, showing stability to thermal decomposition. Broer et al. (1991) studied the polymerization kinetics of a variety of diacrylates (**Y**) in the smectic, nematic, and isotropic states. Here, little difference was observed in the overall kinetics or maximum conversion between the ordered and unordered states, although in the nematic state a slight depression in chain termination by proton transfer was observed.

Much of the complex behavior observed in thermotropic systems can be attributed to the specific chemical structure of the polymerizable mesogen. Instances where the polymerizable groups are placed close to the mesogenic portion of the molecule typically show lower conversion. This is reasonable since the geometrical rearrangements associated with polymerization, such as vol-





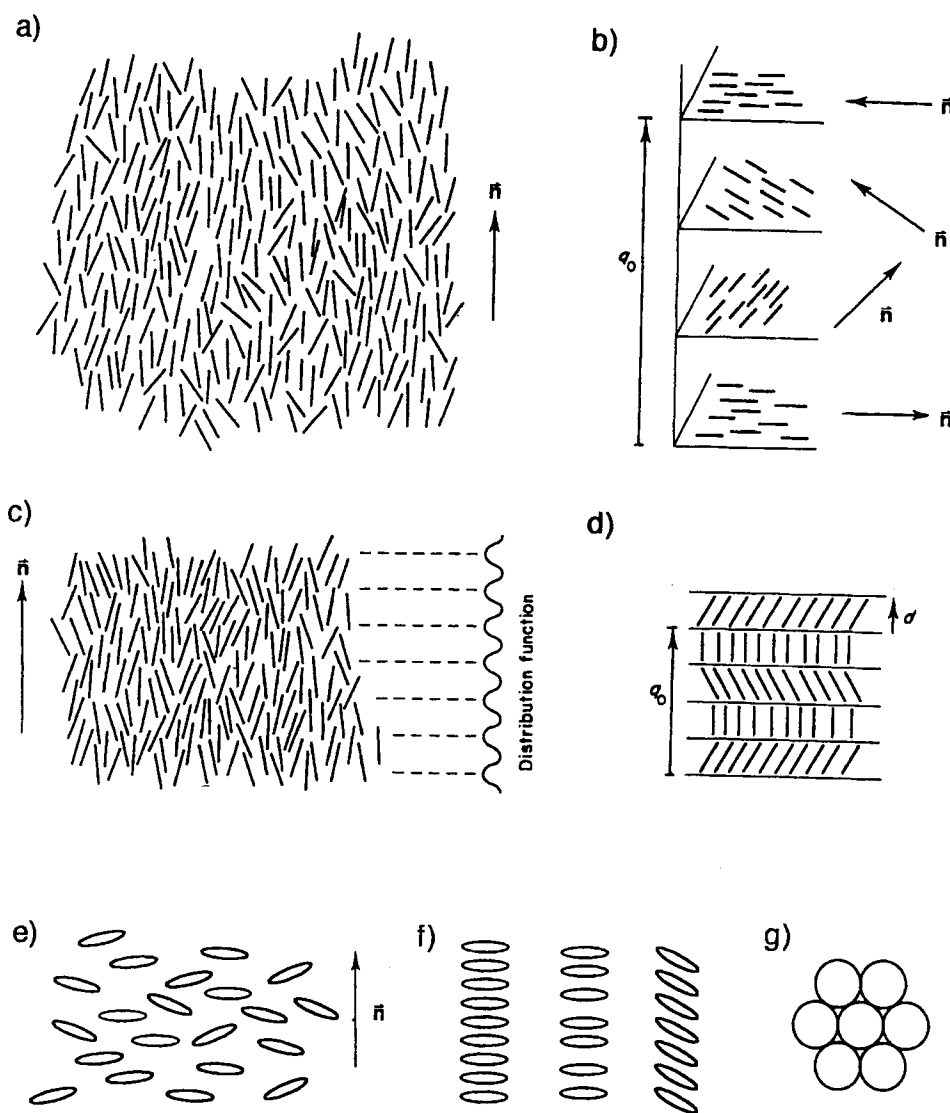
**Figure 15-8.** Schematic diagram of main chain versus side chain liquid crystalline polymers.

umetric contraction, can disrupt the order parameter and mobility, which make the mesophase thermodynamically stable. Due to the connectivity brought about by polymerization, diffusion and packing constraints may or may not be able to maintain the order characteristic of the liquid-crystalline phase. One possible strategy to preserve mesogen order after polymerization is to decouple the mesogenic moiety and polymerizable group with a flexible spacer (i.e., an aliphatic group). Decoupling spacers tend to lower the transition temperature of various phases (Broer et al., 1991), but allow enough molecular motion for polymerization to readily occur without significantly disrupting molecular packing.

The quest of many researchers working on the polymerization of thermotropic liquid crystals is to preserve the anisotropic order of the mesophase after catenation, so that the properties associated with this anisotropy can be accessed outside the stability of the original mesophase. If the polymerization causes a minimal amount of reorganization, the stability of a particular phase can be extended. However, as mentioned above, polymerization can have a destabilizing effect with certain monomer structures (Hikmet et al., 1995). Polymerization of mesogenic monomers in the isotropic state can have mixed effects on the post-polymerization stability of various

phases. Some systems show ordering upon polymerization in the isotropic state when polymerized (Broer et al., 1991; Hikmet et al., 1993; Favre-Nicolin and Lub, 1996; Barclay et al., 1992; Hikmet and Lub, 1995; Spencer and Berry, 1992; Hoyt and Benicewicz, 1990a, b; Favre-Nicolin et al., 1996). This effect can be attributed to either the extension of the mesogenic character of the resulting polymer (as in the case of main chain liquid crystalline polymers), or the result of side chain liquid crystalline polymer formation (see Fig. 15-8) (McArdle, 1989). Other systems show a decrease in mesophase stability with polymerization in the isotropic state due to quenching of the chemical disorder brought on by polymerization (Barclay et al., 1992).

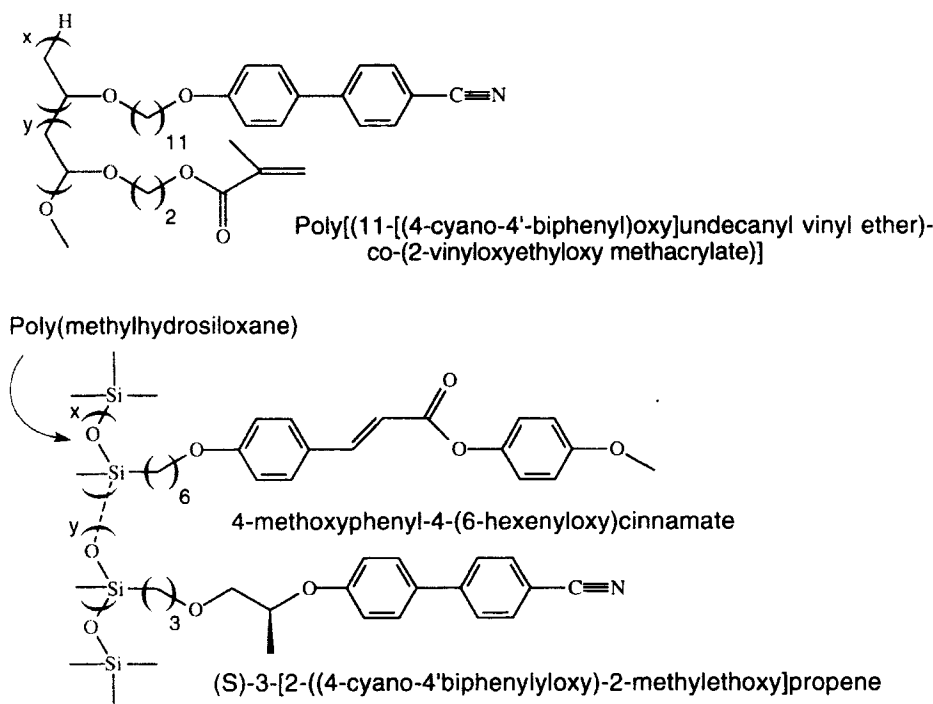
The use of polymerizable groups in stabilization of the ordered phases of thermotropic systems has met with great success in recent years. A large variety of structures show enhanced (or permanent) stability after being reacted in the ordered state. These include nematic (Cambell et al., 1993; Douglas et al., 1994; Hikmet et al., 1993; Barclay et al., 1992; Hoyt and Benicewicz, 1990a, b), cholesteric (Kitzerow et al., 1993), smectic (Hikmet et al., 1995; Hikmet and Lub, 1995; Hikmet and Michielsen, 1995; Stupp et al., 1997a), and discotic (Favre-Nicolin and Lub, 1996; Favre-Nicolin et al., 1996) phases (see Fig. 15-9). This



**Figure 15-9.** Schematic diagram of various thermotropic liquid crystal phases: a) nematic, b) cholesteric, c) smectic (SmA), d) chiral smectic, e) nematic discotic, f) various columnar discotic, g) hexagonal discotic [director ( $n$ ) and helix pitch ( $q_0$ )] [adapted from Leadbetter (1987)].

methodology has also been used to synthesize thermosetting, crosslinked materials which are based on liquid crystalline monomers which are easier to process than their polymeric colleagues (Hoyt and Benicewicz, 1990 a, b). The incorporation of specific chemical functionalities within these stabilized anisotropic phases could

find application in the synthesis of materials with interesting optical (Favre-Nicolin and Lub, 1996), piezoelectric (Hikmet and Lub, 1995), ferroelectric (Hikmet and Michielsen, 1995), pyroelectric (Trollsas et al., 1996 a, b; Mauzac et al., 1995), and mechanical activity (Hikmet et al., 1993; Hikmet, 1991; Lestel et al., 1994).



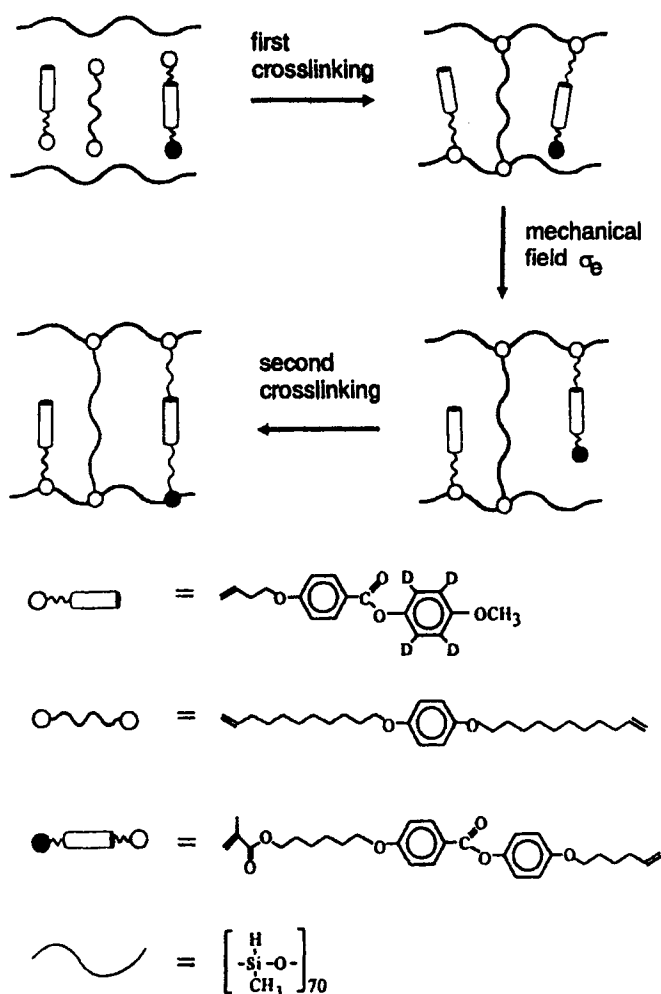
**Figure 15-10.** Polymerizable/crosslinkable side chain liquid crystalline polymers (Chein and Cada, 1994; Percec and Zheng, 1992 b).

There are a number of interesting variations on the common mesogenic monomer structure. The use of liquid crystalline side chain polymers, either with crosslinkable groups or a second polymerizable group, provide another method for the stabilization of anisotropic structures (see Fig. 15-10). These reactions also offer a different opportunity to study polymerization in organized media. Side chain LCPs are known to show a broad range of mesomorphism, but additionally exhibit greater thermal stability as a result of the covalent attachment of mesogens to a backbone (McArdle, 1989). These systems allow the use of different mesogenic and polymerizable side groups (Percec and Zheng, 1992 a, b; Symons et al., 1993; Mauzac et al., 1995), as well as control over the extent of reaction via the content of polymerizable groups within the polymer (Chein and Cada, 1994; Mauzac et al., 1995).

Kuepfer and co-workers developed an elegant elastomeric system based on a siloxane backbone with mesogenic and crosslinkable side chains (Fig. 15-11). These systems can be crosslinked under an external stress, which causes alignment of the mesogenic groups. Crosslinking in the anisotropic state tends to stabilize the nematic phase, while crosslinking in the isotropic state causes nematic destabilization (Disch et al., 1996; Kupfer and Finkelmann, 1994). These observations have been predicted by theory (Warner et al., 1988).

## 15.4 Lyotropic Systems

Unlike thermotropic liquid crystalline systems, order in lyotropic phases is controlled by the chemical structure of the amphiphile and its interaction with a solvent.



**Figure 15-11.** Crosslinkable elastomeric side chain liquid crystalline polymer [used with permission from Disch et al. (1996)].

Amphiphilic molecules are comprised of a hydrophilic and a hydrophobic segment (see Fig. 15-12). In the presence of water or organic solvents, the minimization of unfavorable interactions between the two types of segments or between the segments and solvent cause spontaneous ordering of the system, leading to the compartmentalization of the hydrophobic and hydrophilic portions. The aggregation behavior is dependent, not only on the amphiphile structure, but on the solvent, concentration, and temperature of the system. Low concentrations of amphiphile favor micel-

lar-type aggregation, whereas higher concentrations give rise to a variety of mesophases, which include hexagonal, lamellar, and cubic (see Fig. 15-13) (Laughlin, 1994). Analogous to previous work on thermotropic systems, the polymerization of lyotropic liquid crystals has centered around the stabilizing these ordered structures. Each mesophase has a concentration and temperature window of existence. Polymerization within the system has been extensively investigated as a mode of extending this window; however, the results have been mixed.

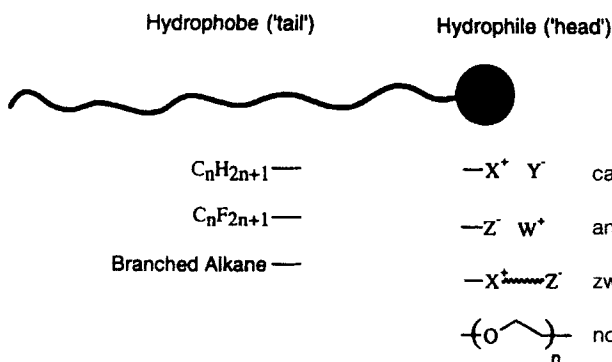


Fig. 15-12. Amphiphile structures.

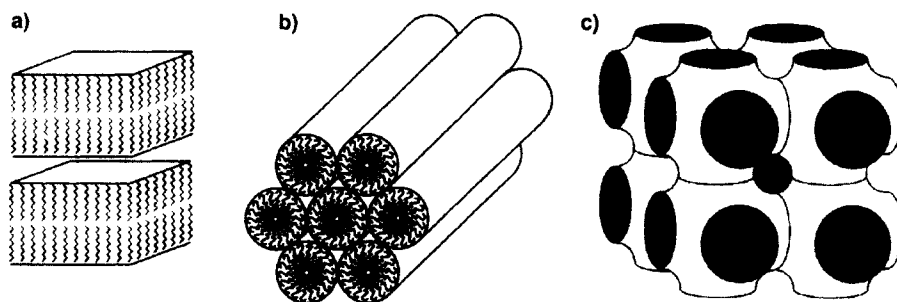


Figure 15-13. Lyotropic mesophases: a) lamellar, b) hexagonal, c) bicontinuous.

Polymerization in lyotropic liquid crystalline phases can be divided into two categories. In one, a mixture of monomer (either hydrophobic or hydrophilic), amphiphile, and solvent is prepared, with the amphiphile serving only to partition the components of the system into an ordered phase. Photopolymerization can be used in these systems (Hohn and Tieke, 1997) with the incorporation of a suitably soluble initiator molecule followed by irradiation (Friberg and Wohn, 1987; Friberg et al., 1993; Laversanne, 1992; Naitoh et al., 1991; Anderson and Strom, 1989). Alternatively, simple thermal initiation is possible provided the mesophase remains stable at the temperature of polymerization (Matsuoka et al., 1992). The kinetics of polymerization seem to be unaffected, behaving much like that of bulk monomers. Under very specific conditions, the resulting polymer can retain the symme-

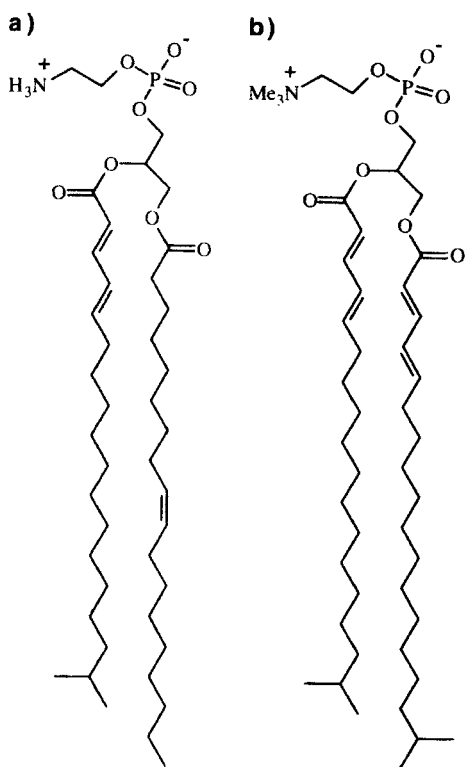
try and dimensions of the original mesophase. This was shown quite dramatically in the work of Anderson and Strom (1989), in which a variety of bicontinuous, three-component systems were polymerized. The product of these polymerizations was a structure with continuous, well-defined nanopores, which replicates the order of the original mesophase. In some cases, these polymerized structures are actually stable after removal of the solvent phase. Complications in the retention of mesophase order upon polymerization in three-component systems can be attributed to two main causes. The first simply results from shrinkage of the monomeric component upon polymerization, which can destabilize the mesophase, causing a change in structure or phase separation (Laversanne, 1992; Naitoh et al., 1991). Complications also arise if the monomer has some co-surfactant properties

which work in concert with the amphiphile. For example, hydrophilic monomers tend to become less hydrophilic upon polymerization, possibly contributing to phase separation (Laversanne, 1992).

The second type of lyotropic system incorporates a polymerizable amphiphile, and as a result, is far more complicated. Included are two-component systems of a polymerizable amphiphile and a solvent (Lee et al., 1995; McGrath, 1996 a, b; McGrath and Drummond, 1996 a; Friberg et al., 1979, 1980; Yang and Wegner, 1982), as well as three-component systems which have both a polymerizable amphiphile, a monomer, and solvent (Hohn and Tieke, 1997; Friberg et al., 1993; Naitoh et al., 1991). Unfortunately, it is very difficult to draw general conclusions concerning polymerization in these systems, but a few remarks can be made. The most important parameters affecting the reaction in these systems and their subsequent behavior are related to the nature and position of the polymerizable group within the amphiphilic structure. In the case of ionic amphiphilic systems, the location of the polymerizable group within the hydrophilic portion tends to cause larger changes upon reaction, presumably due to changes in the head group interactions (including electrostatics and hydration). These changes can be manifested in destabilization of the polymeric system or in simply limiting the degree of conversion achieved (Friberg et al., 1993; McGrath, 1996 a, b). Nonionic systems are less subject to these changes upon reaction, since the hydrophilic moiety is normally spread out over a large portion of the molecule (see Fig. 15-12). Although changes still occur in the cross-sectional area of the head groups upon polymerization, they are typically less disruptive to the mesophase structure. The same is true for ionic systems in which the polymerizable moiety is decoupled from the

ionic center, since the effects of polymerization can be mitigated by flexible spacers. These systems show higher conversion and greater phase stabilization as a result of less head group distortions upon reaction (Naitoh et al., 1991; McGrath, 1996 b; Yang and Wegner, 1992).

The location of the polymerizable moiety within the hydrophobic region of the amphiphilic molecule also has a complicated array of effects dependent on the specific chemical structures involved. In general, the effect of polymerization within the hydrophobic units of a liquid crystal is less disruptive than the polymerization of the hydrophilic units (Friberg et al., 1993; McGrath and Drummond, 1996 a; McGrath, 1996 b). A simple case, studied by Friberg and co-workers, is the polymerization of sodium 10-undecenoate and water. At 60 °C, the amphiphile is readily polymerized within the hexagonal mesophase. The result, however, is an isotropic solution (at 60 °C). Once cooled, the system re-orders into a lamellar phase. Presumably, linking of the hydrophobic chains perturbs the packing enough to destabilize the hexagonal phase relative to a lamellar one (at room temperature) (Friberg et al., 1979, 1980). Undecenyltrimethylammonium bromide, on the other hand, shows less of this destabilizing effect upon polymerization but conversion of the double bond within the hexagonal mesophase is limited to ~40% (McGrath and Drummond, 1996 a). Perhaps a more successful attempt at stabilizing the mesophase structure can be seen in the work of Lee and co-workers. Here, a mixture of polymerizable phosphoethanolamine and phosphocholine amphiphiles (see Fig. 15-14) was polymerized in the bicontinuous phase at 60 °C. Upon cooling, the typical transition of the system to lamellar was not seen. A conversion greater than 80% stabilized the mesophase structure outside its



**Figure 15-14.** Polymerizable a) phosphoethanolamine, b) phosphocholine amphiphiles (Lee et al., 1995).

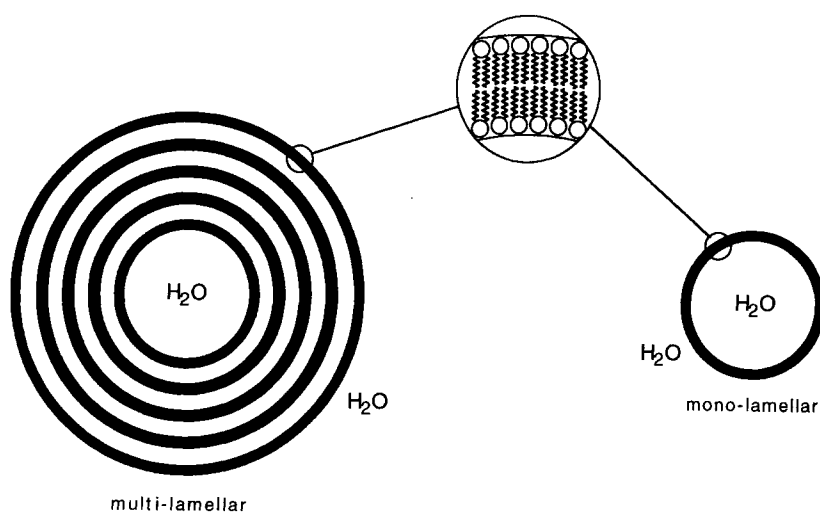
‘normal’ temperature range. Inverse hexagonal phases of these same amphiphiles can undergo polymerization, which stabilizes them against dimensional changes typically associated with changes in temperature (Lee et al., 1995). One hypothesis suggested to predict the stability of a mesophase to polymerization of the hydrophobic moiety considers the packing of hydrophobic chains within the assemblies. If the hydrocarbon chains pack in a crystalline fashion, it is probable that their polymerization will disrupt the mesophase structure. However, if hydrophobe packing is more similar to that of the liquid, it is less likely that polymerization will have an adverse effect on the mesophase (McGrath, 1996 b; McGrath and Drummond, 1996 b). Although this ration-

alization seems plausible, hydrophobe packing is really only one of many factors involved in mesophase stability upon polymerization.

The nature of the polymer chain formed and the changes in packing associated with their linking is of overriding importance in systems with polymerizable amphiphiles. The result of polymerization within the mesophase is a mixture of monomeric and polymeric forms of the amphiphile that depends on the conversion achieved. As a result, the phase behavior of the previously formed polymeric amphiphiles is helpful in predicting the phase changes expected upon polymerization within the mesophase. If an amphiphile concentration can be found that corresponds to the same phase structure (hexagonal, lamellar, etc.) within the monomer/solvent and the polymer/solvent systems, mesophase stability might be predicted through the polymerization reaction. Of course, this thinking is not clearly applicable to amphiphiles with more than one polymerizable unit, or to systems that incorporate monomers in addition to a polymerizable amphiphile.

## 15.5 Vesicles and Bilayers

Unlike the lyotropic liquid crystals discussed previously, bilayers and vesicles are metastable aggregates of amphiphilic molecules dispersed within a solvent. Typically, these nonequilibrium structures are formed by sonication of the amphiphile in solvent, or alternatively by cooling an isotropic solution. Their molecular packing is reminiscent of the lamellar mesophase. The structures consist of molecules assembled into sheets of two molecular layers. In water (the typical media), the amphiphilic molecules are oriented with their hydrophobic portions on the inside of the bilayer, with only the

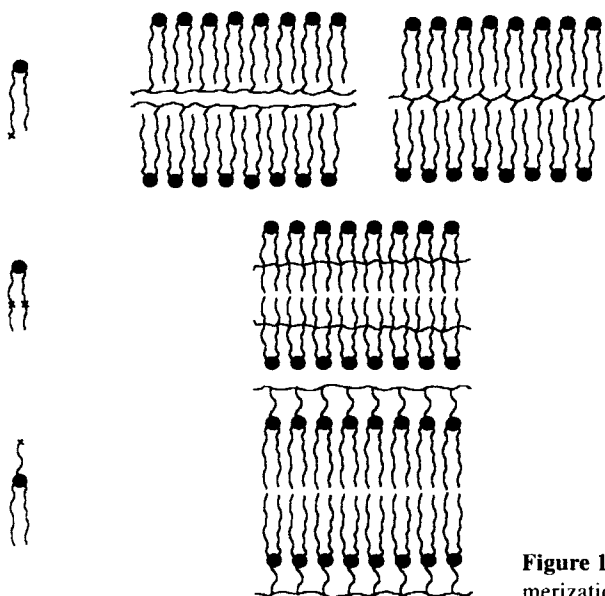


**Figure 15-15.** Vesicle schematic diagram.

hydrophilic portions in contact with water. On the 0.1–1  $\mu\text{m}$  length scale, these bilayers can curve to form totally closed structures (vesicles) or roll up to form tube-like structures. In some cases, vesicles can be made up of multiple bilayers to give an onion-like structure (see Fig. 15-15). Amphiphiles that are conducive to the formation of these bilayer structures have bulky hydrophobic segments, typically consisting of two alkyl chains, or alternatively, a stiff mesogenic segment. These hydrophobes favor aggregations with low curvature, leading to a large lamellar region in the concentration phase diagram of the amphiphile and solvent. As a result, the equilibrium structure of the amphiphiles is typically the lamellar mesophase. With the input of sufficient energy, the system can be coerced into these nonequilibrium structures. The stability of these discrete aggregates is highly dependent on the system, but can last for several months or more (Ringsdorf et al., 1988). The polymerization of vesicles has been investigated as a means to extend the stability and usefulness of these structures.

Vesicles and bilayers are of interest for their potential to form barriers; in applications involving drug delivery, energy conversion, and biomimetic chemistry (Paleos, 1991; Ringsdorf et al., 1988). The bilayer structure slows the diffusion of larger molecules within a system, and the diffusion of hydrophilic molecules is hindered through the interlayer (hydrophobic) region of the structure. These structures are dynamic; amphiphiles readily diffuse within the bilayer as well as exchanging from layer to layer. As a result, the structures lack permanence required for potential applications. Specifically, in the area of drug delivery, vesicles are needed that could sequester a compound throughout processing and implantation, then releasing the drug slowly over time, or in response to an outside stimulus. Another potentially interesting application lies in simulating biological membranes, which could be viewed as complex vesicles, made of amphiphiles, stabilizing proteins, and other macromolecules. The polymerization of simple amphiphiles within the vesicle might provide a route to tailor its barrier





**Figure 15-16.** Possible bilayer structures linked via polymerization (Hedhli et al., 1994; Kunitake et al., 1984).

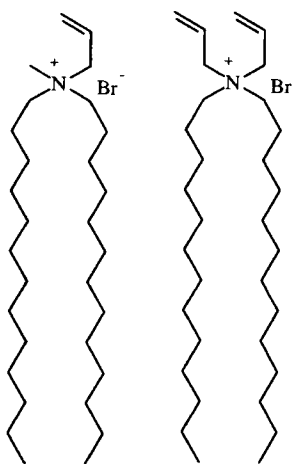
properties and improve the long term stability.

As is typical of polymerization in other ordered systems, the success of stabilizing vesicles and bilayers through polymerization is quite varied. Polymerization has been shown to dramatically increase the shelf life of these nonequilibrium structures, as well as improve their thermal stability (Paleos, 1991; Babilis and Paleos, 1988; Everaars et al., 1996; Lee and O'Brien, 1994). On the other hand, polymerizations within the structure can also destabilize the aggregates, as well as cause phase separation in some instances (Paleos, 1991; Babilis and Paleos, 1988; Everaars et al., 1996; Lee and O'Brien, 1994). Again, the key elements seem to be the structural features of the amphiphile and changes associated with their covalent linking. As in the case of lyotropic liquid crystals, polymerizable groups have been incorporated at different locations in amphiphilic molecules. Polymerization can be accomplished by photoinitiation or by suitable thermal initiators.

The location of the polymerizable group can affect conversion, through steric effects or through the accessibility of the polymerizable group to the initiator (e.g., hydrophobic vs. hydrophilic initiators) (Lee and O'Brien, 1994). Figure 15-16 schematically shows the linking of amphiphiles with polymerizable units placed at different locations. Linking of the amphiphiles at points near the head group greatly reduces their mobility, typically altering their aggregation behavior. Separation of the polymerizable unit from the hydrophilic-hydrophobic junction via a decoupling spacer has been shown to minimize the effects of polymerization (Hedhli et al., 1994; Paleos, 1991; Babilis and Paleos, 1988; Kato and Kunitake, 1991; Kunitake et al., 1989). The location of the polymerizable group within the hydrophobic part can lead to a topochemical-like enhancement of the reaction rates due to the regular arrangement of the polymerizable groups (Borle et al., 1992; Lei and O'Brien, 1994). However, this location of the polymerizable units is complicated by the alkane

melting transition which is seen for many bilayer structures. A sharp, reversible exotherm can be observed in these cases, corresponding to the loss of order within the hydrophobic portion. Polymerization within the hydrophobic portion can lead to the disappearance of this melting transition or its broadening due to added packing frustrations. Polymerization below this melting transition can also limit the degree of conversion due to the lack of mobility of polymerizable units. It is interesting to note the possibility of forming bilayer structures directly from some pre-polymerized amphiphiles; however, their aggregation behavior typically does not match that of the monomers (Kunitake et al., 1984; Paleos, 1991; Elbert et al., 1985). Related to this observation, disordering transitions experienced by vesicles which have been polymerized in situ are often not reversible (i.e., the structure of the polymerized vesicle cannot be completely recovered upon cooling) (Kato and Kunitake, 1991; Kunitake et al., 1989; Meier et al., 1994).

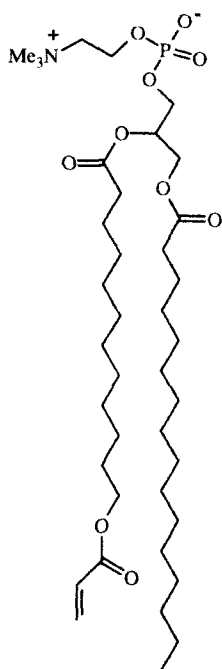
A number of interesting studies have been done to elucidate the structural effects of the amphiphile on the polymerization of vesicles. These studies have centered around both the possibility of stabilizing the structure upon polymerization, as well as on the kinetics of polymerization within these ordered systems. Paleos and co-workers found that vesicles from double chain quaternary ammonium salt amphiphiles with two allyl groups showed enhanced stability upon polymerization induced by gamma irradiation (see Fig. 15-17). However, the mono-allyl-substituted version showed no enhanced stability upon polymerization. NMR evidence of polymerized amphiphiles shows the molecules to be linked in a linear fashion in both cases (rather than cross-linked for the diallyl case), so the differences in their behavior must be particular to the



**Figure 15-17.** Mono- and diallyldidodecylammonium bromides (Paleos, 1991).

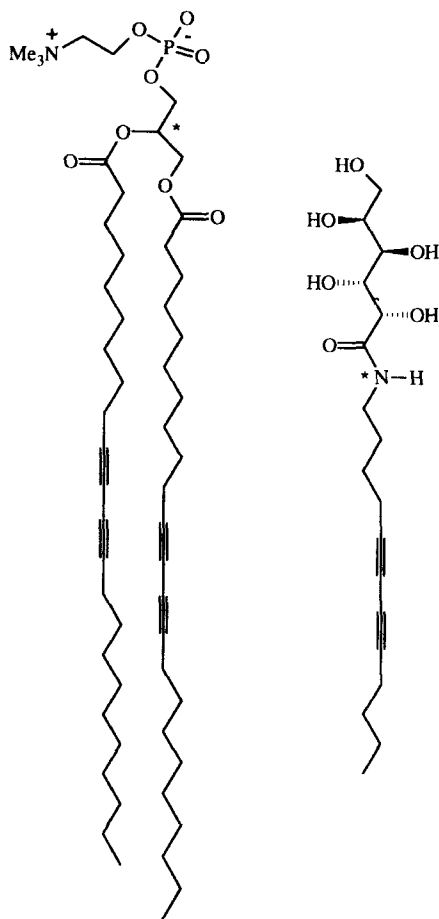
structure of the polymer backbone formed (Babilis et al., 1985). A number of researchers have looked extensively into amphiphiles with polymerizable head groups, especially the effects of decoupling segments between the hydrophobe, hydrophile, and polymerizable groups (Kunitake et al., 1984, 1989; Kato and Kunitake, 1991; Elbert et al., 1985). In the area of kinetics, O'Brien and co-workers carried out a number of studies on free-radical polymerizations in phosphocholine-based amphiphiles (Fig. 15-18). For amphiphiles with polymerizable groups in their tail portions, they found solution-like polymerization rates at low conversions. At high conversion, however, decreasing mobility in the system causes primary termination to dominate (Sells and O'Brien, 1994; Elbert et al., 1985).

A related topic of interest is the polymerization of diacetylene-containing amphiphiles. These amphiphiles are able to pack in highly ordered bilayer structures due to the rigidity of the hydrophobic segment. Some diacetylene-containing amphiphiles assemble into typical bilayer structures; however, their polymerization (via irradiation) usually leads to dramatic changes in

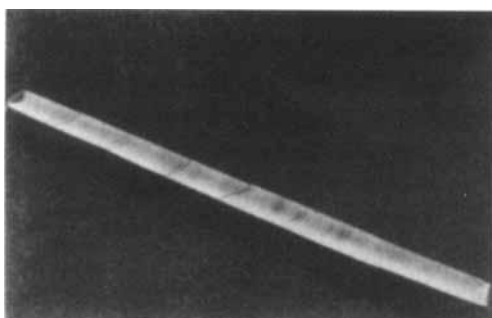


**Figure 15-18.** Acryloyl-substituted phosphocholine (Sells and O'Brien, 1994).

packing due to the backbone rigidity (Everaars et al., 1996). At the very least, a large change in the melting transition is seen on polymerization. Often, polymerization causes the complete disappearance of this transition (Paleos, 1991). A variety of diacetylene-containing amphiphiles have been shown to form more complicated bilayer structures upon cooling below the alkane melting transition (or by slowly precipitating from solution) (see Fig. 15-19) (O'Brien, 1994; Schnur, 1993; Rudolph, 1988; Georger et al., 1987; Fuhrhop et al., 1991; Frenkel and O'Brien, 1991; Peek et al., 1994). Depending on the method of preparation, ribbons and tubules can be formed with diameters of  $\sim 0.5 \mu\text{m}$  and lengths of up to  $1000 \mu\text{m}$  (see Fig. 15-20). Remarkably, many of these structures are retained upon polymerization of the diacetylenes (Georger et al., 1987; Fuhrhop et al., 1991; Frenkel and O'Brien, 1991).



**Figure 15-19.** Tubule-forming diacetylene amphiphiles (O'Brien, 1994).



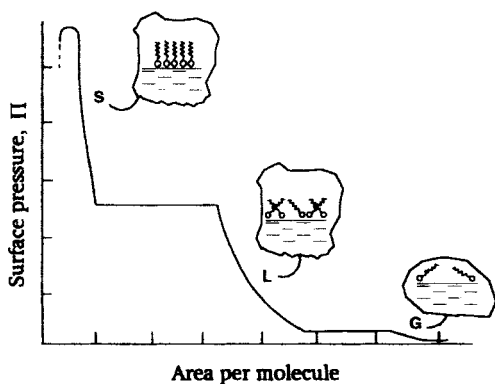
**Figure 15-20.** Electron micrograph of a diacetylene amphiphile tubule [used with permission from Schnur (1993)].

## 15.6 Langmuir–Blodgett Films

The polymerization of mono- and multilayer structures assembled by the Langmuir–Blodgett (LB) technique has been investigated for a number of years. This technique involves isolating a collection of amphiphilic molecules at the interface between a liquid and a gas. Under appropriate conditions, these molecules will self-assemble into a well-organized monolayer based on their dual nature. Monolayers can be further utilized on the ‘trough’ or deposited by passing a substrate through the liquid–gas interface. By sequentially dipping a substrate, it is often possible to build up multilayer structures (Petty, 1996). As in the polymerization of other organized media, the objective is to stabilize the ordered structure, providing a useful material. Applications are far reaching, including separation membranes, adhesives, nonlinear optical films, and well-defined insulating layers. As in other systems discussed thus far, the success achieved in the quest for stabilized ordered structures is highly dependent on the chemical structure of the amphiphile. The incorporation of polymerizable or crosslinkable groups is possible in the hydrophilic portion of the amphiphile (Tsibouklis et al., 1991), as a counter ion to a charged hydrophilic moiety (Higashi and Niwa, 1993), within the hydrophobic portion (Furlong et al., 1993; Shibasaki et al., 1994; Fukuda et al., 1989; Saito et al., 1996; Mathauer et al., 1995; Seufert et al., 1995) or by intercalation within a multilayer of unpolymerizable amphiphilic molecules (Rosner and Rubner, 1994; Park et al., 1996). Polymerizable groups which have been incorporated are widely varied, including diacetylenes, vinyls, and acrylates, to name a few. Typically, polymerization is initiated by exposure to UV or another radiation source (Liu et al., 1994). However, initiators in the subphase have been

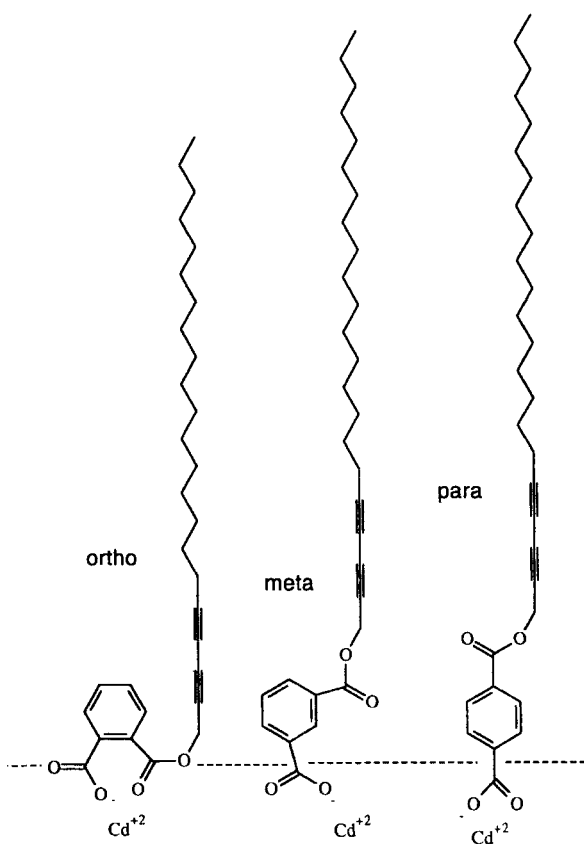
used in some cases (Zhou and Duran, 1992; Zhou et al., 1990; Duran and Zhou, 1992).

As in the polymerization of other ordered systems, the stabilization of these structures is difficult due to the shrinkage or reorganization of the monomers upon polymerization. In LB mono- and multilayers, the packing of the system is highly dependent on the dimensions and conformation of these molecules. Changes in either of these on polymerization typically lead to dramatic changes in the film structure and characteristics. Two avenues exist by which this dilemma can be circumvented. Firstly, the decoupling of the polymerizable moiety from the structural features of the amphiphile that control packing can allow reorganization of the molecular conformation with minimal disruption of the film (Kruchinin et al., 1994; Arslanov, 1992). Secondly, it is possible that the polymeric material can form a stable monolayer on its own, which might allow the retention of the macroscopic order within the film (Shibasaki et al., 1994; Arslanov, 1992). The study of polymerization within this type of ordered structure is further complicated by the LB process itself. The structure of the floating monolayer is highly dependent on the subphase on which it rests (often doping of the subphase with specific salts can result in changes in the hydration of the amphiphile head group) (Furlong et al., 1993). In addition, molecular packing is highly dependent on the pressure exerted, showing regimes of two-dimensional gas, liquid, and solid (see Fig. 15-21). The kinetics of polymerization and the overall extent of reaction tend to be very dependent on molecular packing. In the case of LB layers on a substrate, the specifics of molecular packing are also a function of numerous variables associated with their deposition, including the mode of dipping, dipping speed, and substrate type (Arslanov, 1992; Dhanabalan et al., 1996).



**Figure 15-21.** Surface pressure versus area per molecule isotherm: S) solid 'condensed' phase, L) liquid 'expanded' phase, and G) 'gaseous' phase [adapted from Petty (1996)].

A number of LB polymerizations have centered around diacetylene-containing amphiphiles. In many cases, the order of these molecules in the LB layer is conducive to their topochemical-like reaction (Furlong et al., 1993; Fukuda et al., 1989; Saito et al., 1996; Liu et al., 1994; Kruchinin et al., 1994; Dhanabalan et al., 1996; Tsibouklis et al., 1993). The polymerization of 10,12-pentacosadiynoic acid is a good example. Multilayer polymerization by exposure to UV radiation shows conversion to a colored film (blue), indicative of the conjugated poly(diacetylene) backbone. Typically, coupled with polymerization there are changes in the tilt angle which the molecules make with the layer normal, and, as a result, changes in the layer thickness (Saito et al., 1996; Dhanabalan et al., 1996; Tsibouklis et al., 1993). The polymerized films keep their layered structure; however, cracks can develop as a result of domain formation upon polymerization. The critical role of molecular packing can be seen in the polymerization study of heneicosa-2,4-diynyl carboxybenzoates on an aqueous  $\text{CdCl}_2$  subphase by Furlong and co-workers (see Fig. 15-22). Here, variations in the ring sub-



**Figure 15-22.** Heneicosa-2,4-diynyl carboxybenzoates on an aqueous  $\text{CdCl}_2$  subphase (Furlong et al., 1993).

stitution show large changes in reactivity due to the resultant packing. Specifically, the ortho conformation polymerizes readily, whereas the meta and para showed very little reactivity, presumably due to the interaction of the hydrophilic portion of the amphiphile and the subphase (Furlong et al., 1993).

A number of papers have been published in the last few years in which the organization of the LB mono- and multilayers has been exploited in an attempt to make materials with highly anisotropic conductivity. Two strategies have been employed to confine a conductive component within the plane of a multilayer structure. The most di-

rect method is the incorporation of a suitable monomer (e.g., pyrrole, aniline, thiophene) within the amphiphile head group. For example, 2-pentadecyl aniline can be polymerized as a monolayer by adding sulfuric acid and ammonium peroxydisulfate to the subphase solution (Zhou and Duran, 1992; Zhou et al., 1990; Duran and Zhou, 1992). An anisotropically conductive material could be prepared, presumably by consecutive deposition of these layers. An alternative method involves LB multilayers of alkane acids and  $\text{FeCl}_3$ . These multilayers are then alternatively exposed to HCl and pyrrole vapor. Pyrrole is spontaneously polymerized within the hydrophilic regions of the structure upon contact with the  $\text{FeCl}_3$ . These materials have shown conductivity anisotropies of several orders of magnitude (Rosner and Rubner, 1994; Park et al., 1996; Cheung et al., 1990).

Another strategy for the production of stabilized, ordered multilayer films is in the reaction of two different components within the structure. Octadecyl esters of L-lysine and L-glutamic acid formed fully miscible monolayers when compressed on an LB trough. Multilayers of these amphiphiles were readily polymerized by heating between 30 and 50°C, although it is not clear how well the layered structure survives this reaction (Fukuda et al., 1989). Similarly, multilayers of a mixture of vinyl stearate and octadecyl acrylate polymerize readily upon UV exposure, even though pure vinyl stearate monolayers show low conversion (Fukuda et al., 1989). Multilayer structures built with consecutive dipping of different monolayers offers the possibility of building composite structures. The use of alternating monolayers of amine- and acid-based amphiphiles can allow the covalent linking of individual layers, although reactions between layers have not been well characterized (Tsiboukis et al., 1991, 1993).

## 15.7 Intercalated Systems

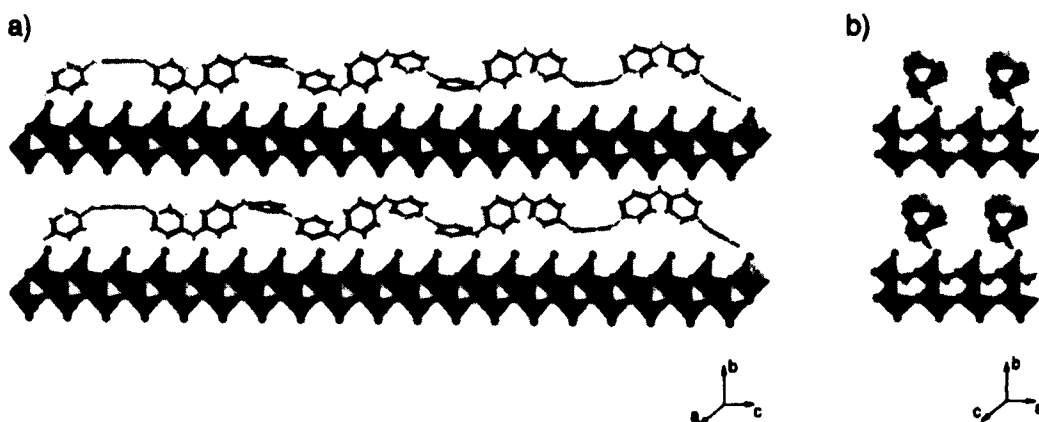
A number of naturally occurring inorganic materials contain well-defined layers or channels. These include clays (fluorohectorite, montmorillonite, and perovskites), metal phosphates [ $\text{VOPO}_4$ ,  $\text{H}_2\text{O}_2\text{PO}_4$ ,  $\text{Zr}(\text{HOPO}_3)_2$ ,  $\text{Ti}(\text{HOPO}_3)_2$ ], metal oxides, and sulfides ( $\text{V}_2\text{O}_5$ ,  $\text{FeOCl}$ ,  $\text{MoO}_3$ ,  $\text{MoS}_2$ ,  $\text{TaS}_2$ ). These materials are composed of covalently bonded layers associated through weaker van der Waals and hydrogen bonding forces. The interlayer space can be occupied by charge balancing ions, water, or neutral species. Zeolitic materials (zeolite Y, mordenite, mesoporous silicates, and others) offer a similar gallery structure based on a three-dimensional lattice with a wide range of pores and/or channels. The incorporation of organic molecules within the voids of these structures has been investigated for quite some time. Intercalation methodologies have centered around vapor or solution exposure of the host material to the guest species. The actual incorporation of the guest can be through the exchange of charge balancing ions or by simple adsorption within the host. Polymerization within these hosts provides the opportunity to fashion highly ordered composite materials with a minimum of processing. Interesting properties result from the confinement of the organic material to the molecular dimensions of the host pore structure, including enhanced thermal stability, changes in electrical activity, as well as changes in mechanical relaxations.

The majority of work concerning polymerization within intercalation systems centers around monomers that form conjugated polymers such as aniline, pyrrole, and thiophene. The interest is in the synthesis of composites containing an inorganic material and a conducting polymer. In the case of insulating host materials (the majority), the

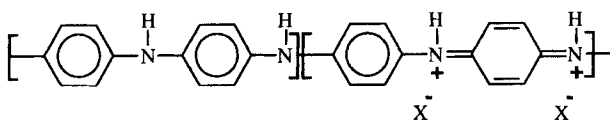
potential result is highly anisotropic conductors. In the case of layered hosts, high conductivities in the plane of the layers result, with insulating properties perpendicular to the host layers (due to the boundary between conducting elements). Also of interest are the conductivities of these polymers when confined to molecular dimensions, since the conductivity has been attributed to electron delocalization within the bulk polymers, not only along single chains, but between chains as well (Mehrotra and Giannelis, 1991; Enzel and Bein, 1989; Wu and Bein, 1994). Typical syntheses involve the solution intercalation of aniline or pyrrole into the host system. Polymerization proceeds by exposure to a suitable oxidizer, such as  $\text{Cu}^{+2}$  (Nakajima and Matsubayahi, 1993, 1995),  $\text{Fe}^{+3}$  (Kerr et al., 1996), ammonium peroxodisulfate (Enzel and Bein, 1989; Wu and Bein, 1994; Chao et al., 1993; Liu and Kanatzidis, 1993; Uma and Gopalakrishnan, 1995) and  $\text{O}_2$  accompanied by heat (Liu and Kanatzidis, 1995; Liu et al., 1993). Some hosts are able to polymerize the monomers in situ due to the high oxidation potential of intralayer atoms or balancing ions, causing concurrent intercalation and polymerization (Mehrotra and Giannelis, 1991; De Stefanis et al., 1995; Roque et al., 1993; Kanatzidis et al., 1987, 1989, 1990). For example, Kanatzidis and co-workers have demonstrated the ability of  $\text{V}_2\text{O}_5$  xerogel to oxidize a number of monomers, producing conducting polymers in the interlayer space directly upon intercalation (Liu et al., 1993; Kanatzidis et al., 1987, 1989, 1990).

The actual polymerization of these monomers within the interlayer spaces of a host material has not been studied extensively. Isolation of the resulting polymer from the composite structure (usually by acid digestion of the host) has shown sluggish conversion of the monomer. Typically, this

is attributed to the slow diffusion of outside oxidizing agents into the intercalation structure (Mehrotra and Giannelis, 1991; Enzel and Bein, 1989; Chao et al., 1993; Uma and Gopalakrishnan, 1995; Liu et al., 1993; Kanatzidis et al., 1989). There has been a number of interesting studies on the structure of the final composite materials, mostly centered around the conformation of the polymer within the host. The polymer has been found to adopt an extended molecular conformation due to confinement. Observations of the primary layer spacings, before and after intercalation and polymerization, suggest the inserted polymer layer corresponds to the width of one molecule in most cases. Kerr et al. (1996) propose a helical conformation for intercalated poly(aniline) within the layered structure of  $\text{MoO}_3$ , based on both crystallographic and modeling data (see Fig. 15-23). In principle, the extended conformation of these polymers should lead to enhanced conductivities due to greater delocalization along their chains. The conductivity of the resulting composites, however, varies considerably. Other issues of importance are the volume fraction of polymer, specific polymer–host interactions, and percolation of the conducting component. For many conducting polymers, the actual conductivity is a function of the doping level as well as their conformation. In the case of poly(aniline), the conductivity depends on protonation, as well as its level of oxidation. Its incorporation within an acidic host or exposure to another proton source will cause the formation of the “emeraldine salt” form responsible for conduction (see Fig. 15-24) (Enzel and Bein, 1989). Loadings of 20 wt.% or more in a mesoporous silicate<sup>1</sup> have yielded bulk conductivities of only  $10^{-8}$  S/cm (isolated polymer  $\sim 10^{-2}$  S/cm), as a result of encapsulation of the polymer component within the insulating host (Wu and Bein, 1994). However,



**Figure 15-23.** Possible poly(aniline) conformation in  $\text{MoO}_3$  lattice: a) viewed along  $[100]$ , b) viewed along  $[001]$  [used with permission from Kerr et al. (1996)].



**Figure 15-24.** Emeraldine salt form of poly(aniline).

poly(aniline) loadings of 17.5 wt.% in  $\text{Cu}^{+2}$ -exchanged fluorohectorite exhibit a conductivity of 0.05 S/cm in the plane of the layers after exposure to HCl vapor ( $10^{-7}$  S/cm perpendicular to the layers) (Mehrotra and Giannelis, 1991). Lastly, the intercalation of a conducting polymer within an electrically active host can reveal interesting conductivity versus temperature behavior due to changes in the nature of charge transport within the separate components, for example, the incorporation of polypyrrole in Fe- $\text{OCl}$  (Kanatidis et al., 1987) or polyaniline in  $\text{V}_2\text{O}_5$  xerogel (Kanatidis et al., 1990).

Far fewer studies have been conducted on nonconducting polymers within a host system. Clay-PMMA intercalation compounds were synthesized by the emulsion

polymerization of methyl methacrylate in the presence of montmorillonite. However, the polymerization does not selectively deposit in the interlayer; hence the synthesis requires washing the majority of the polymer from the exterior of the clay layers (Lee and Tang, 1996). Poly(acrylonitrile) has also been formed within the interlayer of montmorillonite by gamma irradiation of the vapor intercalated monomer. Subsequent thermal treatment can convert the polymer to highly oriented graphite (Yamanaka et al., 1974; Kyotani et al., 1988). Polymerization within zeolitic hosts has been studied more from the standpoint of catalyst poisoning, rather than composite synthesis. The oligomerization of various monomers within the structure of molecular sieves blocks the pores and ruins their catalytic activity (Richardson et al., 1990; Pereira et al., 1991).

<sup>1</sup> The mesoporous silicate MCM-41 was used in this study. Mesoporous silicates have zeolitic-like structures with nanometer porosity.



## 15.8 Thermodynamics/Kinetics

The thermodynamics of polymerization within ordered systems has not been investigated very thoroughly, however, there are some general considerations that can be enumerated. The change in free energy of a system upon polymerization is due to both enthalpic and entropic terms. The enthalpy changes associated with the conversion of monomeric units to a polymer show little variation with ordering, reflecting, for example, the difference in energy associated with a double bond and a single bond. However, the ordering of monomeric units will significantly impact the entropic terms within the free energy equation. The process of linking monomers to form a polymer severely limits their mobility. In particular, isotropic polymerization causes the loss of much of the system's translational entropy (the vibrational and rotational components of the monomer and polymer are quite similar) (Odian, 1991). Entropy changes associated with polymerization in ordered monomeric units will be substantially lower, since the entropy of those systems is already less than that of the isotropic state. Obviously, the difference in entropy relative to the isotropic state is a function of the order parameter and geometry of the system. The order inherent in the systems previously discussed varies widely, from topochemical systems in which monomers have no translational entropy to liquid-crystalline systems, which have two degrees of translational entropy.

Much more has been published on the kinetics of polymerization within ordered systems. In particular, there has been a number of studies on the conversion rates for monomers in both LB layers and lipid bilayers. The study of LB monolayers is aided by the ease at which the polymerization rates can be monitored through barrier movement

at some constant applied surface pressure. Bodalia and Duran studied the oxidative polymerization of 2-pentadecylaniline as a function of the applied surface pressure, the temperature, and the monomer concentration. They found the polymerization to follow Arrhenius' law

$$K = A e^{(-E_a/RT)}$$

In addition, they observed that the activation energy ( $E_a$ ) of polymerization was very close to that of the bulk case and was independent of the applied surface pressure (within the liquid regime), indicating that ordering of the monomers had little effect on their reaction pathway. However, the rate of the polymerization ( $K$ ) was enhanced over the bulk case. This was attributed to an increase in the pre-exponential factor ( $A$ ) within the rate law, reflecting a decrease in the freedom available to the reactants and activated complex in comparison to the isotropic case (Bodalia and Duran, 1993; Bodalia et al., 1994).

The pre-exponential factor includes variables associated with the collision factor, which reflects, among other things, the sterics associated with the polymerization process (i.e., the approach of a polymer end and a monomer unit). In this case, the confinement of the polymerizable units within a compressed LB monolayer enhanced their reactivity by limiting the conformations that could be explored. Unfortunately, ordering of the monomeric units would seem to have an unpredictable effect on the monomer sterics. Ordering could serve to either help or hinder polymer to monomer approach, depending on the specific packing prevailing in the system. This effect will also vary greatly with the degree of order within the system. Systems such as lyotropic liquid crystals, in which the order away from the hydrophilic/hydrophobic junction approaches the liquid-like state, will probably

not show an enhancement of the polymerization rate. On the other hand, highly ordered systems such as compressed LB layers can show rate enhancements due to favorable ordering of monomer units (a topochemical-like effect) (Arslanov, 1992) or limited reactivity with unfavorable packing (Furlong et al., 1993; Fukada et al., 1989; Kruchinin et al., 1994).

Most work on kinetics within ordered systems centers around the rate of polymerization and the molecular weight of the resulting polymer. The effect of ordering within these systems is most often in the suppression of chain termination via coupling and disproportionation mechanisms due to low translational mobility. This effect is similar to the 'gel effect' observed in most bulk polymerizations, where increasing viscosity limits the diffusion of the growing chain at higher conversion. In the free-radical polymerization of phosphatidylcholine derived bilayer assemblies, the polymerization rates ( $R_p$ ) were found to obey typical solution dependencies on monomer and initiator concentrations at low conversion

$$R_p \propto [M][I]^{0.5}$$

At high conversions, however, polymerization rates reflect the dominance of primary termination over bimolecular termination mechanisms (coupling or disproportionation), approaching

$$R_p \propto [M]^2 [I]^1$$

At least in these instances, the propagation rate constants do not seem to be affected by the ordering of the system probably due to the liquid-like order within the layers (Sells and O'Brien, 1994; Lei and O'Brien, 1994). The ordering of monomer units can also have a detrimental effect on the overall polymerization rates, due to the inability of the monomer to diffuse to the growing chain

ends. In some highly ordered thermotropic systems, depressed conversion rates have been attributed to poor alignment of the polymerizable units and low mobilities within the system (Spencer and Berry, 1992).

## 15.9 Two-Dimensional Products from Ordered Media

A very interesting polymerization in an organized environment is one occurring in the confinement of a two-dimensional space. This polymerization is interesting because the reaction among monomers in this environment could form, in principle, polymers with two-dimensional (2D) architecture. 2D polymers represent a significant departure from the best known architecture for macromolecules, namely, that of linear chains and all their derivatives, such as rings, ladders, combs, branched chains, and 3D networks. A 2D environment is defined here as a Cartesian volume with two large and one small dimension. If monomers connect covalently within this  $x, y, \gg z$  volume, the macromolecules produced have 2D architecture only if their 2D shapes persist after geometrical confinement has disappeared. This flat shape may be an equilibrium conformation or one that is kinetically trapped over infinite time scales.

Throughout this century, polymer science has studied the linear chain and its architectural derivatives, and most theories and synthetic methodologies revolve around the concept of a 1D covalent backbone. Furthermore, the technology of polymeric materials takes advantage primarily of the ability of these 1D objects to entangle with each other, align uniaxially under mechanical forces, or fold into interconnected thin crystals. Having access to 2D polymers, other scientific and technical opportunities may

emerge. One example would be the stacking of these flat, molecular objects to form materials with chemically well-defined and temporally stable surfaces. Other possibilities, predicted theoretically, envision the reversible thermal folding of flat molecular sheets (Abraham and Nelson, 1990a, b; Abraham and Kardar, 1991; Morse et al., 1992; Kantor and Kremer, 1993; Mori and Wadati, 1993). With this concept the 2D polymers could be imagined functioning in the controlled delivery, removal, or transient masking of substances.

Alternatively, 2D polymers could mechanically reinforce linear polymers, or function as the precursors to tubular, covalent structures by spontaneous or induced "rolling" transitions. In order to bring these ideas to fruition, bulk polymerization reactions must be developed which yield architecturally 2D polymers. The ideal bulk polymerization would be one in which neat monomer could be converted to 2D polymer. Our laboratory was the first to report such reactions (Stupp et al., 1993a, b, 1995; Huggins et al., 1997). Preceding our work, many methodologies had been invented to confine monomers in two dimensions using externally controlled confinements, or by dispersion in a nonsolvent. Furthermore, many of these 2D polymerizations do not yield architecturally 2D polymers, but networks or linear chains which become globular structures when 2D confinement disappears. Some of these previous efforts are discussed below.

### 15.9.1 Two-Dimensional Confinement of Monomer

Many methodologies have been invented to confine monomers in two dimensions prior to polymerization. For example, efforts have been directed at the polymerization of amphiphiles that form layered struc-

tures when dispersed in water (Lei and O'Brien, 1994; Hub et al., 1980; Dorn et al., 1984; Sakada and Kunitake, 1989; Asakuma et al., 1991; Kuo and O'Brien, 1991; Gros et al., 1981; Fendler and Tundo, 1975; Regen et al., 1984; Lee and O'Brien, 1994). In other work, monomers have been confined at oil-water interfaces to form infinite networks (Rehage et al., 1988; Dubault et al., 1975). The air-water interface offered by a Langmuir trough has also been used as a confining environment for monomers (Day et al., 1979). Langmuir-Blodgett films and self-assembling monolayers (SAMs) are also potentially useful systems for 2D polymerizations (see Sec. 15.6). The polymerization of monolayers with conventional reactive groups presents rather serious steric challenges. This is the case because van der Waals distances are greater than the length of covalent bonds formed in conventional addition polymerizations involving double bonds. This problem was solved in the bulk 2D polymerizations developed by Stupp and co-workers either by the use of bilayers or by molecular design using multiple planes of reaction within the 2D volume. This way, the individual covalent backbones formed to stitch the 2D structure need not be very long at all, but may in fact be rather short (see next section).

As mentioned previously, once in 2D confinement the monomers can polymerize, but synthesis of a 2D polymer of finite dimensions is not easily achieved. The formation of a 2D polymer would require monomers that have more than one polymerizable function per molecule, and also monomers that have molecularly rigid structures. This essentially prevents the collapse of the structure to globular shapes having comparable, *x*, *y*, and *z* dimensions. 2D polymerizations in which the environment confining monomers is never removed may find application in the fabrication of future devic-

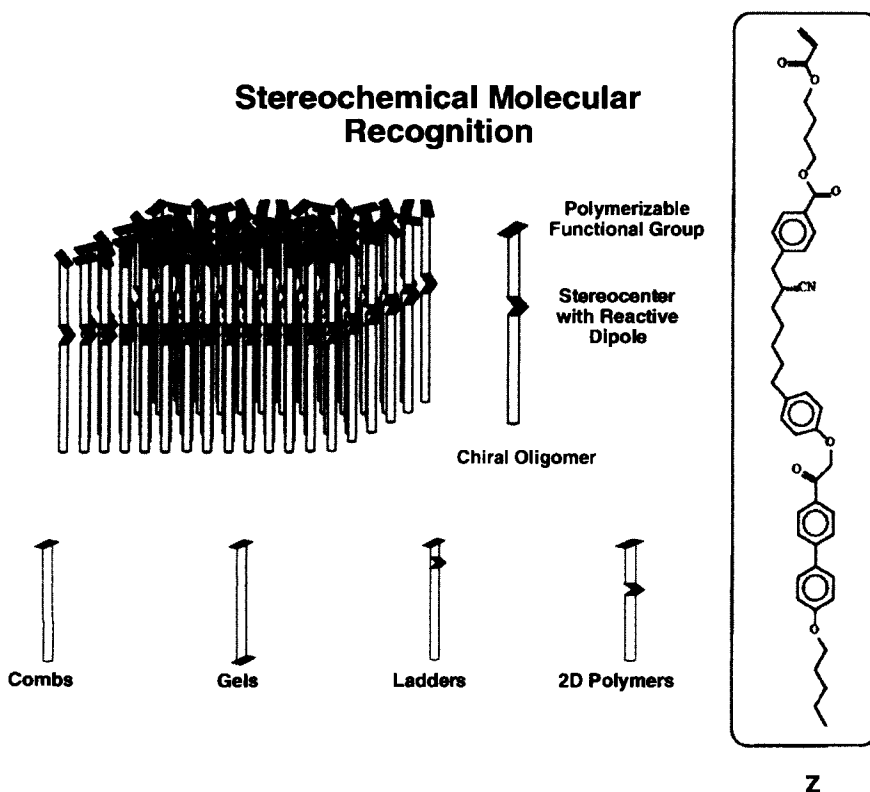
es, but they would obviously not be useful for the bulk synthesis of 2D polymers as materials. In the next section, we describe the first examples of bulk synthesis of 2D polymers from neat monomer using self-assembling reactive molecules.

### 15.9.2 Two-Dimensional Polymers from Self-Assembling Monomers

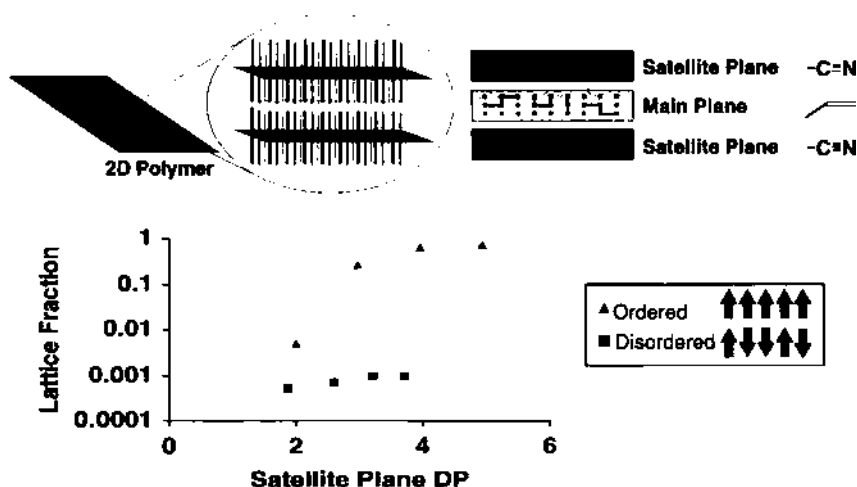
The bulk synthesis of 2D polymers requires monomers that are structurally programmed to self-organize into planar assemblies which are not destroyed by polymerization reactions. The authors' laboratory reported in 1993 the first bulk synthesis of 2D polymers. In this approach molecule **Z**, synthesized through 21 steps, was used to create flat polymers (Stupp et al.,

1995). As depicted in Fig. 15-25, this synthesis is based on the reaction among orientationally ordered monomer molecules in layers analogous to those found in smectic phases. However, the orientational order, not always found in common smectic phases, is critical to achieve the reaction among monomers to form high molecular weight 2D polymers.

The ideal layered assembly of molecules to form 2D polymers in a bulk reaction needs to contain molecules that have more than one reactive group. In the case of **Z**, acrylate and nitrile groups served as the polymerizable entities. If molecules of the assembly had only one polymerizable moiety or two placed at the termini of molecules, reaction would lead to combs or gels, respectively. The molecular design of precur-



**Figure 15-25.** Molecular recognition approach to two-dimensional polymers.

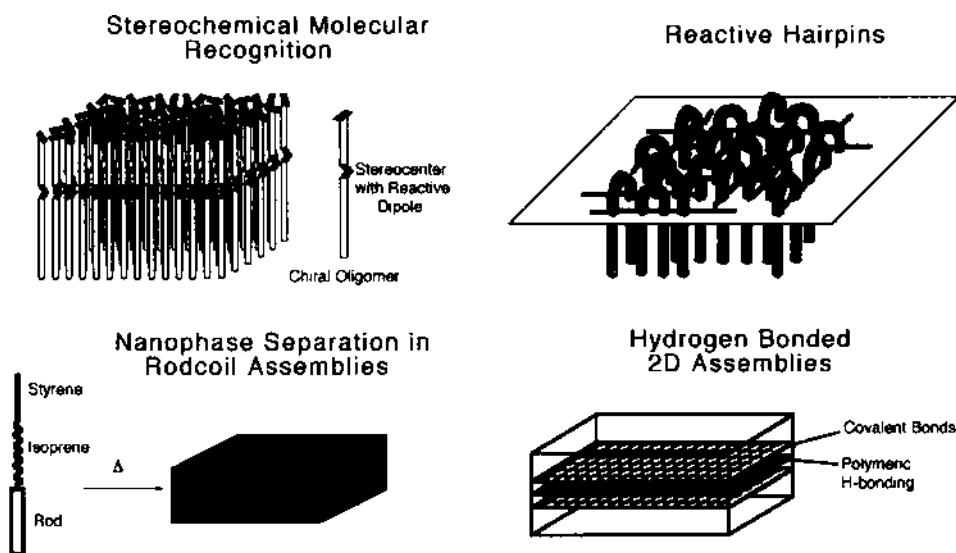


**Figure 15-26.** Computer simulation of 2D polymer growth. The graph plots the logarithm of the fraction of precursor molecules connected by random walks within an orientationally ordered and a randomly ordered bilayer assembly (Stupp et al., 1995).

sors with two reactive groups, but one not positioned at the terminus of the molecule, is certainly more challenging, since functional groups away from the terminus would tend to disrupt the self-organization into layered structures. Furthermore, the two functions must be separated by distances that avoid the correlation of polymerizing paths, otherwise 1D ladder polymers would form. In the case of **Z**, the product is a bilayer 2D polymer, since one reactive function is positioned at the terminus of the molecules. This approach led successfully to the formation of 2D polymers in a test tube containing melted monomer, implying its bulk nature. The reader is referred to the literature for the characterization of the products obtained (Stupp et al., 1993 a, b, 1995).

We believe orientational order in the layered assembly was critical in forming high molecular weight products. This concept was demonstrated by our laboratory with a computer simulation which evaluated the extents of reaction and average degrees of polymerization necessary to form

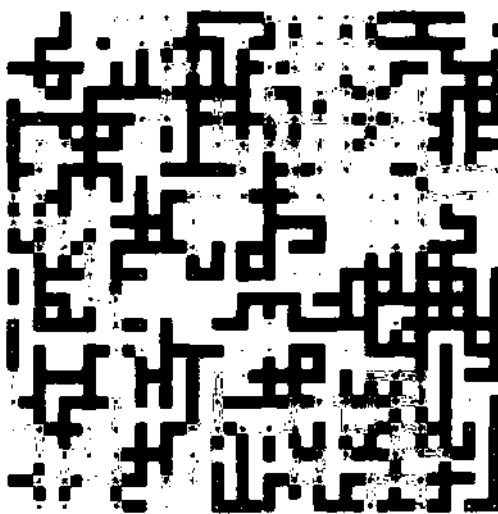
2D polymers (Stupp et al., 1995). The results of this simulation, explained in Fig. 15-26, indicate that only a small number of precursor molecules needs to be connected by a given stitching reaction (covalent bond forming) in order to form large 2D molecular objects. This simulation used random walks to represent the path of polymerization among monomers connecting on three different planes of reaction. Applied to the polymerization of bilayers of **Z**, these planes represent two planes in which nitrile groups react with each other (satellite planes), and a third in the middle of the bilayer containing the acrylate groups (main plane). Using parameters found experimentally, this simulation shows that only short backbones (e.g., tetramers) are necessary in the satellite planes to connect orientationally ordered monomers into large 2D objects. Interestingly, this is not the case when monomers are orientationally disordered within the layer. Thus molecular recognition processes that orient neighboring monomers in parallel orientation are important for an efficient reaction. In the experimental



**Figure 15-27.** Approaches to the polymerization of two-dimensional objects.

system, we believe this parallel orientation is favored by homochiral interactions among stereocenters containing the highly dipolar nitrile groups. A different group also concluded, based on the application of percolation theory to our experimental system, that sufficient extents of reaction had been achieved to form large 2D objects (Munkel and Heerman, 1993).

Since the original report, three other approaches to the bulk formation of 2D polymers by self-organizing monomers have been developed by our laboratory. These other approaches are summarized in Fig. 15-27. One very useful approach involves the use of triblock oligomers which self-assemble into nanophase separated layers. The middle in this case contains unsaturated groups (e.g., isoprene units) which can thermally react to stitch the layers into 2D polymers (Stupp et al., 1993 b). Figure 15-28 describes a simulation of 2D polymer formation using these self-assembling triblock molecules. Another approach has been to design reactive molecules that fold into hairpins and organize into layers.



**Figure 15-28.** Cross section of simulated 2D polymerization involving rodcoil molecules. If reactive segments contain an average of seven polymerizable structural units, only 30% must react to form a 2D object.

The hairpins connect by a polymerization reaction among identical groups in both arms of the hairpin, and the folded backbone connects molecules into a 2D object. Experimentally, we developed such a system

using diacetylene chemistry (Son, 1994). Finally, we recently reported on 2D polymers formed by a combination of covalent bonds and hydrogen bonds (Huggins et al., 1997). The attractive feature of these systems is the possibility of transforming them thermally from 2D to 1D structures reversibly. There is no question that many more systems remain to be developed to generate 2D polymers in organized media. Novel catenating reactions for monomers that do not disrupt the 2D confinement will make an important contribution to this area.

### 15.10 Nanostructures via the Polymerization of Supramolecular Units

One of the great challenges for 21st century chemistry will be the synthesis of molecular nanostructures as functional compounds or constituents of supramolecular materials (Stupp et al., 1997a). For this purpose, the nanostructures could have either the broad or narrow distributions of molar mass which are characteristic of polymeric molecules. Using conventional organic chemistry, it will be difficult in the near future to achieve the synthesis of objects ranging in size between a few and one hundred nanometers. One possibility is the use of dendrimers (Moore, 1996), but these macromolecules may limit the accessible shape and chemical structure, since very specific monomers are required for their synthesis. Sizes may also be limited, since their chemical perfection drops rapidly after many generations. On the other hand, hyperbranched polymers of narrow distribution will remain an interesting route to molecular nanostructures. Nature of course forms nanostructures by synthesizing 1D chains with specific chemical sequences which find energy minima, folding into objects of specific shape.

This may someday be possible with synthetic linear polymers.

A different approach to nanostructures is offered by supramolecular chemistry using molecules programmed to form finite objects with nanoscale dimensions. Our laboratory discovered a methodology to obtain these nanostructures by self-assembly with molar masses greater than 100 000 daltons and narrow size distributions. Specifically, we reported on a family of mushroom-shaped objects formed by precursors referred to as rodcoil molecules (Stupp et al., 1997a, b, 1998; Tew and Stupp, 1998; Tew et al., 1998; Whitaker et al., 1998). A fascinating prospect for stable nanostructures are confined polymerizations within the nanoscale environment of such supramolecular units. These polymerizations have to initiate, propagate, and terminate within the very small dimensions of spontaneously formed molecular aggregates. Great hope for the future in this approach is offered by a recent discovery in our laboratory. We have identified systems in which polymerization is confined within anisotropic, internally organized aggregates created by spontaneous self-assembly. Interestingly, these aggregates can contain dozens of monomers and molar masses of the order of 70 000 daltons with polydispersities of only 1.1 (Zubarev and Stupp).

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## 16 Biocatalytical Routes to Polymers

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## List of Symbols and Abbreviations

$M_w$	weight-average molecular weight
$M_n$	number-average molecular weight
$n$	degree of polymerization (DP)
$T_g$	glass transition temperature
$T_m$	melting temperature
$V_{max}$	reaction velocity obtained under saturating concentration of substrate
AFM	atomic force microscopy
Ala	alanyl
AOT	bis(2-ethylhexyl)sodium sulfosuccinate
Asn	asparaginy
Asp	aspartyl
ATP	adenosine triphosphate
BOD	billirubin oxidase
CA	<i>Candida antartica</i>
CC	<i>Candida cylindracea</i>
$\epsilon$ -CL	$\epsilon$ -caprolactone
CoA	coenzyme A
CP/MAS	cross-polarization/magic angle spinning
Cys	cysteiny
DDL	12-dodecanolide
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulfoxide
DP	degree of polymerization
DSC	differential scanning calorimetry
Gln	glutaminy
Glu	glutamyl
Gly	glycyl
GTP	guanosine triphosphate
HRP	horseradish peroxidase
IR	infrared
LB	Longmuir–Blodgett
Leu	leucyl
Met	methionyl
mRNA	messenger RNA
NADP	nicotinamide adenine dinucleotide phosphate
NADPH	reduced NADP
NMR	nuclear magnetic resonance
PDL	15-pentadecanolide
PF	<i>Pseudomonas fluorescens</i>
PHA	poly[( <i>R</i> )-hydroxyalkanoate]
PHB	poly[( <i>R</i> )-3-hydroxybutyrate]
Phe	phenylalanyl
PPL	porcine pancreatic lipase

PVME	poly(vinyl methyl ether)
RNA	ribonucleic acid
SBP	soybean peroxidase
Ser	seryl
TEM	transmission electron microscopy
Thr	threonyl
tRNA	transfer RNA
Tyr	tyrosyl
Val	valyl
$\delta$ -VL	$\delta$ -valerolactone

## 16.1 Introduction

Enzymes have several remarkable catalytic properties, such as high catalytic power and selectivity under mild reaction conditions, especially in comparison with other chemical catalysts. In the field of organic synthesis, enzymes have often been employed as catalysts with the result that highly selective organic reactions have been developed and in certain cases, functional materials have been produced (Whitesides and Wong, 1985; Jones, 1986; Klibanov, 1990; Santaniello et al., 1992).

The production of all naturally occurring polymers is *in vivo* catalyzed by enzymes. Recently, reports on the *in vitro* synthesis of not only biopolymers but also nonnatural synthetic polymers through enzymatic catalysis have appeared (Ritter, 1993; Kobayashi et al., 1994a, 1995). These enzyme-catalyzed polymerizations have received much attention as a new methodology for polymer syntheses. Polymers with new structures became synthetic targets and required the development of highly selective enzymatic polymerizations. This way the increasing demand for the production of functional polymers for materials science could be met.

The present chapter deals with recent advances in biocatalytical routes to polymers, i.e., polymerizations catalyzed by an enzyme ("enzymatic polymerizations"). Generally, there are three classes of polymer synthesis catalyzed by an enzyme:

- (1) Enzymatic synthesis *in vivo* (in living cells) via biosynthetic pathways.
- (2) Enzymatic synthesis *in vitro* (outside cells) via biosynthetic pathways.
- (3) Chemical synthesis *in vitro* (in test tubes) via nonbiosynthetic pathways catalyzed by an isolated enzyme.

The first part of this chapter briefly reviews *in vivo* and *in vitro* biosyntheses of poly-

mers which belong to classes (1) and (2), respectively (Watson et al., 1987). The second part deals with the chemical synthesis of polymers via nonbiosynthetic pathways catalyzed by an isolated enzyme [class (3)].

## 16.2 Biosynthetic Pathways to Polymers

Recently, *in vivo* and *in vitro* biosyntheses of polypeptides and *in vivo* biosynthesis of polyesters have been extensively studied in view of materials science. Here the biosynthesis of polymers that are natural and nonnatural will be presented.

### 16.2.1 Polypeptides

Living organisms can be regarded as protein synthetic machinery, where RNA maintains a catalytic function. The biosynthesis of artificial polypeptides has been achieved by the expression of target proteins in living cells by using a gene recombination technique. Natural and nonnatural polypeptides have been synthesized *in vitro* by a cell-free translation system in a test tube.

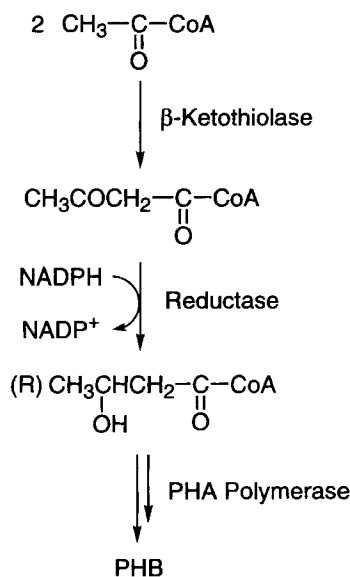
Artificial proteins are expected to constitute a new class of polymeric materials with precise control of the chain length, sequence, and stereochemistry. By using genetic engineering, periodically sequence-regulated polypeptides  $[(\text{AlaGly})_x\text{ZGly}]_n$  ( $\text{Z} = \text{Ala, Asn, Asp, Glu, Leu, Met, Phe, Thr, Tyr, and Val}$ ) are prepared (Krejchi et al., 1994; Deguchi et al., 1994; Cantor et al., 1994; Yoshikawa et al., 1994). For the synthesis of target periodic polypeptides, a DNA sequence encoding the polypeptide is determined by employing a genetic code. The enzymatic polymerization of the DNA monomer (oligonucleotide) affords DNA multimers, from which the target length

DNA is fractionated and cloned in an expression vector. The cloning of the recombinant expression vector in an *E. coli* strain produces the target polypeptide. In using high cell density cultures of recombinant *E. coli*, the multi-gram scale biosynthesis of poly(L-alanylglycine) is achieved (Panitch et al., 1997). The biosynthesis of proteins is extended to the preparation of polypeptides containing a photofunctional nonnatural amino acid (Hohsaka et al., 1993, 1994 a, b, 1996).

A large scale in vitro synthesis has been successfully achieved. Continuous flow of the buffer feed, including amino acid, adenosine triphosphate (ATP), and guanosine triphosphate (GTP), in the system of prokaryotic or eukaryotic origin and continuous removal of the reaction products afford cell-free polypeptide production (Spirin et al., 1988). In using MS2 phage RNA or brome mosaic virus RNA4 as the template, 100 copies of polypeptide per mRNA molecule can be produced in 20 h. A pyridine-catalyzed system of polypeptide synthesis simply composed of ribosome, aminoacyl-tRNA, and template is proposed (Nitta et al., 1994). In this system, chemical energy sources, such as ATP and GTP, and soluble protein factors are not required.

### 16.2.2 Polyesters

A wide variety of microorganisms produce optically active poly[(*R*)-3-hydroxybutyrate] (PHB) and accumulate it as carbon and energy storage materials. Recently, PHB has received much attention as biodegradable and biocompatible thermoplastics. PHB is prepared from acetyl-coenzyme A (acetyl-CoA) by a sequence of three



Scheme 16-1.

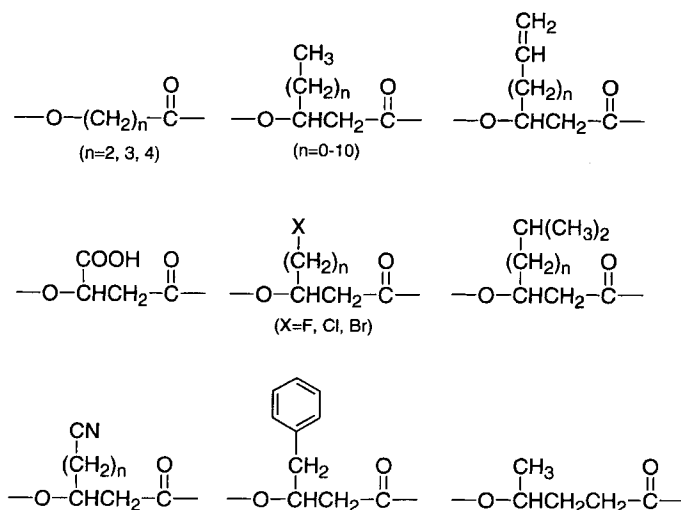


Figure 16-1. Unit structures of typical biopolyesters.



enzymatic reactions (Scheme 16-1). The key enzyme is PHA polymerase, which catalyzes the polymerization of (*R*)-3-hydroxybutyryl-CoA.

Combinations of a variety of carbon source and enzyme origin afford various nonnatural copolyesters, which contain a 3-hydroxyalkanoate unit having functional groups in the side chain (Holmes et al., 1981; Holmes, 1985; Doi et al., 1987 a, b; Doi, 1995; Anderson and Dawes, 1990; Steinbüchel and Schlegel, 1991; Steinbüchel and Valentin, 1995; Lee, 1996). Units of 4-hydroxybutyrate or 5-hydroxyvalerate can be incorporated in the copolymer. Typical examples of biopolyester units are shown in Fig. 16-1.

## 16.3 Chemical Synthetic Pathways to Polymers Using Isolated Enzymes

### 16.3.1 Polysaccharides

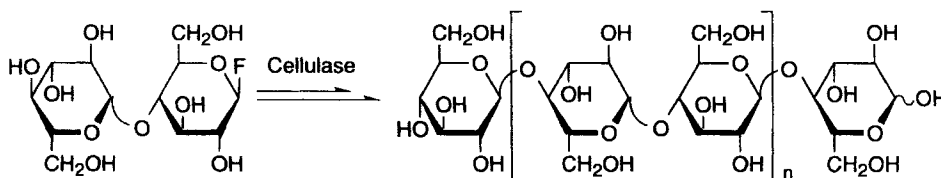
It is generally accepted that an enzymatic reaction is virtually reversible, and hence the equilibrium can be controlled by varying the reaction conditions. Based on this concept, hydrolases, i.e., enzymes which catalyze a bond-cleavage reaction by water, have been used as catalysts for the reverse reactions of hydrolysis, leading to polymer production by a bond-forming reaction.

Glycosidases are expected to construct a selective glycosidation by utilizing their characteristic enzymatic catalysis under ap-

propriate conditions. Glycosyl fluorides are known to be recognized by glycosidases.  $\beta$ -Cellobiosyl fluoride is polymerized by using cellulase derived from *Tricoderma viride*, an extracellular hydrolytic enzyme of cellulose, in a mixture of acetonitrile and acetate buffer (pH 5) to produce synthetic cellulose (Scheme 16-2) (Kobayashi et al., 1991, 1992 a, 1993). This is the first example of cellulose synthesis via a nonbiosynthetic path. X-ray and CP/MAS solid  $^{13}\text{C}$  NMR analyses show that the crystal structure is cellulose II, a thermodynamically more stable form. The enzyme promotes transglycosylation of the cellobiosyl moiety toward the 4'-hydroxy group of another monomer involving the elimination of hydrogen fluoride. In this polymerization, regio- and stereoselectivities are perfectly controlled.

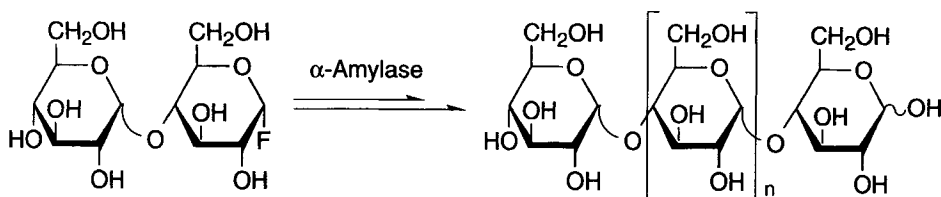
Formation of the stereoregular  $\beta(1 \rightarrow 4)$  linkage is explained by the formation of a glycosyl-enzyme intermediate at an active site of cellulase with elimination of the fluoride anion, followed by the attack of the 4'-hydroxyl group of another monomer or propagating polymer located in a subsite of the enzyme to this reactive intermediate and leading to the stereoregular formation of  $\beta(1 \rightarrow 4)$  linkage. Synthetic cellulose and cellooligomers are also synthesized by the enzymatic polymerization of cellotriosyl fluoride and cellotetraosyl fluoride (Osada et al., 1995).

The process of synthetic cellulose formation is visually analyzed using transmission electron microscopy (TEM) (Kobayashi



Scheme 16-2.

*synthetic cellulose*



Scheme 16-3.

et al., 1994 b). Cellulose formation is detected as early as 30 s after the initial stage of the reaction in the aqueous acetonitrile. Irregular aggregates of cellulose are formed at the boundary of the micellar particles, suggesting the occurrence of the polymerization at the interface of the micelle. The used cellulase is a mixture of many cellulolytic and noncellulolytic enzyme components. In using the purified cellulase (39 kDa), fibril materials are obtained. The electron diffraction pattern of the product shows the formation of metastable cellulose I with a parallel orientation; this is an allomorph of natural cellulose, which has long been believed to be impossible to obtain by an artificial process (Lee et al., 1994). Based on these results, a new concept of "choroselectivity", i.e., selectivity concerning the relative ordering of the polymer chain direction, in polymerization chemistry has been proposed (Kobayashi and Shoda, 1995; Shoda and Kobayashi, 1995; Kobayashi et al., 1996 a).

Enzymatic polymerization of 6- and 6'-monomethylated cellobiosyl fluoride monomers using the purified cellulase has been examined (Shoda et al., 1994; Okamoto et al., 1997). The 6-*O*-methylated monomer polymerizes smoothly in a regio- and stereoselective manner to give a novel cellulose derivative having a methyl group alternately at the 6-position, which can never be realized by the conventional modification of natural cellulose, i.e., the methylation of cellulose. On the other hand, the polymerizability of the 6'-*O*-methylated

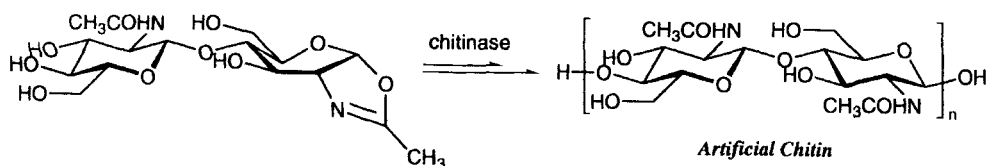
monomer is relatively low. The difference in the polymerization behavior may be due to the steric repulsion between the methyl group of the monomers and the acceptor site of the cellulase catalyst.

Enzymatic polymerization of  $\alpha$ -D-maltosyl fluoride using *Aspergillus oryzae*  $\alpha$ -amylase catalyst in an aqueous methanol produces a maltooligosaccharide of DP up to 7 (Scheme 16-3) (Kobayashi et al., 1992 b). Formation of the stereo- and regioselective  $\alpha(1 \rightarrow 4)$  glycosidic bond is explained by a mechanism involving double inversion of the C1 carbon configuration of the monomer.

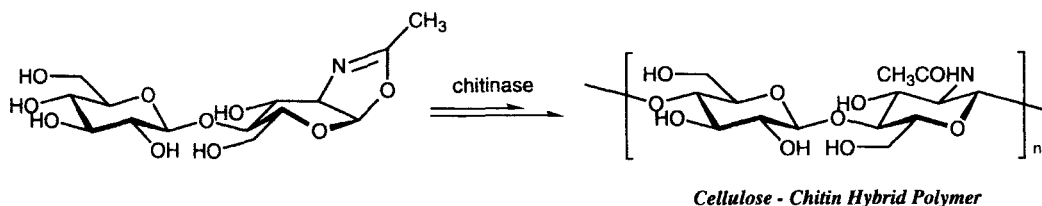
$\alpha$ -D-Maltosyl fluoride is enzymatically converted to give cyclodextrin and maltooligosaccharides by cyclodextrin- $\alpha(1 \rightarrow 4)$  glucosyltransferase catalyst (Treder et al., 1986). Enzymatic transglycosylation of  $\alpha$ -D-maltosyl fluoride with a cyclodextrin using pullulanase or isoamylase as the catalyst produces a branched cyclodextrin, 6-*O*- $\alpha$ -maltosylcyclodextrin (Kitahata et al., 1987; Yoshimura et al., 1987).

Artificial xylan is prepared by the cellulase-catalyzed polymerization of  $\beta$ -xylobiosyl fluoride (Kobayashi et al., 1996 b). The polymerization proceeds in a perfect regio- and stereoselective manner. The synthetic xylan consists exclusively of a xylopyranose moiety connected through a  $\beta(1 \rightarrow 4)$  glycosidic bond, whereas naturally occurring xylan contains L-arabinose and 4-*O*-methylglucuronic acid as minor unit in the side chains.

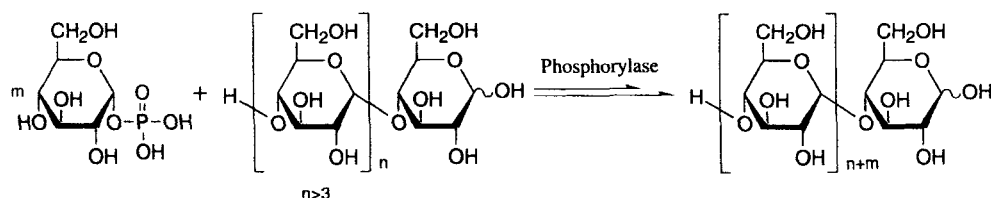
Hemithiocellodextrins having 4-thiocellobiosyl repeating units linked by  $\beta(1 \rightarrow 4)$



Scheme 16-4.



Scheme 16-5.



Scheme 16-6.

oxygen linkages are synthesized by the cellulase-catalyzed polycondensation of 4-thio- $\beta$ -cellobiosyl fluoride (Moreau and Driguez, 1996). Polymerization in the aqueous acetonitrile produces a water-soluble product with DP up to 20.

A sugar oxazoline derivative derived from di-*N*-acetylchitobiose is subjected to enzymatic polymerization using chitinase (*Bacillus* sp.) as catalyst (Scheme 16-4) (Kobayashi et al., 1996c). This monomer polymerizes in the presence of catalytic amounts of chitobiose to give a water-insoluble chitin with molecular weight of  $4.6 \times 10^4$ . From the oxazoline from *N*-acetylglucosamine, chito-oligosaccharides are enzymatically obtained. This is the first example of the enzymatic polyaddition of sugar oxazoline derivatives by a hydrolytic enzyme.

A nonnatural polysaccharide having a glucose unit and an *N*-acetylglucosamine unit alternately in the main chain is synthesized by chitinase-catalyzed polyaddition of a new disaccharide monomer in a buffer (Scheme 16-5) (Makiguchi et al., 1996). The resulting polymer can be regarded as a hybrid polymer of cellulose and chitin.

Lysozyme-catalyzed polymerization of *N*-acetylchitobiose in an acetate buffer containing 30% ammonium sulfate at 70 °C produces useful chito-oligosaccharides (Usui et al., 1990). The high concentration of ammonium sulfate effectively induces the transglycosylation to give hexa-*N*-acetylchitohexanose and hepta-*N*-acetylchitoheptanose. D-Glucose is enzymatically converted to gluco-oligosaccharides using almond  $\beta$ -glucosidase (Ravet et al., 1993). In using a high concentration (7.5 M) of the mono-

mer, di-, tri-, and tetrasaccharides are obtained.

Phosphorylase is well known to catalyze the polymerization of  $\alpha$ -D-glucose-1-phosphate in the presence of primer, leading to in vitro synthesis of amylose (Scheme 16-6) (Cori and Cori, 1940). This reaction has been expanded to the enzymatic synthesis of star- and comb-shaped amylose (Ziegast and Pfannemüller, 1987), styryl-type amylose macromonomer (Kobayashi et al., 1996e), and poly(dimethylsiloxane)-graft-amylose (Braunmühl et al., 1995).

### 16.3.2 Polypeptides

As seen for the hydrolysis enzyme, proteases catalyze not only the hydrolysis of peptide bonds but also peptide bond formation. The reaction of amino acid esters in the presence of some proteases produces water-insoluble products. From L-methionine methyl ester, an oligopeptide with a DP of 8–10 is obtained by using papain catalyst (Sluyterman and Wijdens, 1972; Jost et al., 1980; Komatsu et al., 1995). Esters of phenylalanine, threonine, tyrosine, and glutamic acid are also subjected to the protease-catalyzed oligomerization (Anderson and Luisi, 1979; Aso et al., 1988).

In order to enhance the molecular weight of the polypeptide, an enzyme is modified to show high catalytic activity in an aqueous DMF solution by a mutation technique (Wong et al; 1990). A subtilisin mutant (subtilisin 8350), derived from BPN' (subtilisin from *Bacillus amyloliquefaciens*) via a six site-specific mutant (Met 50 Phe, Gly 169 Ala, Asn 76 Asp, Gln 206 Cys, Tyr 217 Lys, and Asp 218 Ser), induces the polymerization of L-methionine methyl ester in aqueous DMF, yielding polymer with a DP up to 50. Another mutant (subtilisin 8397), which is the same as 8350 without changing Tyr 217, is used as a catalyst for the poly-

merization of single amino acid, dipeptide, and tripeptide methyl esters (Zhong et al., 1991).

A different type of peptide hydrolase, dipeptide transferase, catalyzes the oligomerization of a dipeptide amide. From glycyl-L-tyrosinamide, the formation up to octamer is observed (Heinrich and Fruton, 1968).

### 16.3.3 Polyesters, Polycarbonates, and Polyamides

Lipase and esterase are enzymes which catalyze the hydrolysis of esters in an aqueous environment. Some of them can act as a catalyst for the reverse reactions, esterification and transesterification, in an organic medium. These catalytic actions have been expanded to the enzymatic synthesis of polyesters. So far, different modes of polymerization have been demonstrated: the polycondensation of oxycarboxylic acid derivatives and combinations of dicarboxylic acid derivatives/glycols, poly(addition-condensation) of a cyclic acid anhydride and glycols, and ring-opening polymerization of lactones.

As for oxyacid monomers, 10-hydroxydecanoic acid was first used for lipase-catalyzed polymerization. The monomer is polymerized in benzene using soluble poly(ethylene glycol)-modified lipase to give an oligomer with a DP of more than 5 (Ajima et al., 1985). The polymerization of ricinoleic acid proceeds using lipase from *Candida cylindracea* (lipase CC) or *Chromobacterium viscosum* as a catalyst in water, hydrocarbons, and benzene to give polymer with a molecular weight of around  $1 \times 10^3$  (Matsumura and Takahashi, 1986). Glycolic acid and its ethyl ester are converted into the corresponding oligomer by lipase or esterase catalysis (Ohya et al., 1995). 10-Hydroxydecanoic and 11-hydroxyundecanoic acids are also enzymatically polymer-

ized to give the corresponding polyesters (O'Hagan and Zaidi, 1993, 1994). A large amount of lipase CC (10 times the weight of monomer) is necessary to obtain relatively high molecular weight polyesters.

Crude porcine pancreatic lipase (PPL) catalyzes the polymerization of methyl 6-hydroxyhexanoate (Knani et al., 1993). The polymer with a DP up to 100 is synthesized by polymerization in hexane at 69 °C for more than 50 days. PPL-catalyzed polymerization of methyl 5-hydroxypentanoate for 60 days produces the polymer with a DP of 29. An optically active oligomer is obtained by the enantioselective polymerization of racemic methyl 6-hydroxyheptanoate in the presence of PPL catalyst (Knani and Kohn, 1993), whose enantioselectivity is not high (<40%).

Various combinations of dicarboxylic acid derivatives and glycols enzymatically afford polyesters under mild reaction conditions. *Mucor miehei* lipase immobilized on a macroporous anion exchange resin induces the polycondensation of adipic acid and 1,4-butanediol (Binns et al., 1993). A horizontal, two-chamber reactor is employed to facilitate the use of the molecular sieves. A low dispersity ( $M_w/M_n = 1.1$ ) polyester with DP=20 is obtained by the two-stage polymerization. When a vacuum system is used to remove the water formed during the esterification, the molecular weight increases up to  $4.2 \times 10^4$  (Wang et al., 1996). In the case of the lipase-catalyzed polymerization of dicarboxylic acid dimethyl ester with glycol, there is an equilibrium between the polymer and the monomers. Nitrogen bubbling removes the formed alcohol, leading to a quantitative conversion of the monomer (Mezoul et al., 1995a).

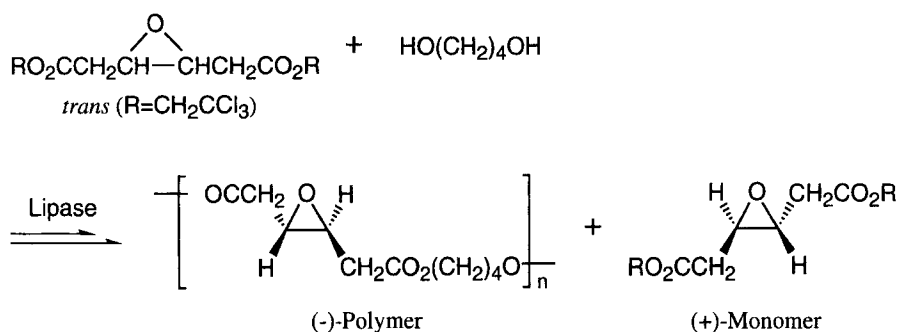
Dehydration polymerization of a dicarboxylic acid and a glycol proceeds in an aqueous medium by using lipase catalyst to produce an aliphatic polyester (Kobayashi

et al., 1997a). The enzyme origin and monomer structure affect the yield and molecular weight of the product polyester. This is the first clear-cut evidence of the dehydration polymerization in water.

Activated esters such as 2,2,2-trichloroethyl, 2,2,2-trifluoroethyl, and vinyl esters show high reactivity toward lipases and have been used as monomer for enzymatic polycondensations. Aliphatic polyesters with molecular weights of several thousand are obtained by PPL-catalyzed polycondensation of bis(2,2,2-trichloroethyl) or bis(2-chloroethyl) alkanedioates with glycols (Wallace and Morrow, 1989a; Linko et al., 1994). The vacuum method is useful for the enhancement of the molecular weight (Brazwell et al., 1995; Linko et al., 1995). The PPL-catalyzed polymerization of bis(2,2,2-trichloroethyl) adipate with 1,4-butanediol in supercritical fluoroform produces a low dispersity polyester ( $M_w/M_n < 1.1$ ) (Chaudhary et al., 1995). The molecular weight of the synthesized polymer can be controlled by changing the pressure.

Dicarboxylic acid divinyl esters are also available as monomer for enzymatic polycondensation with  $\alpha,\omega$ -glycols (Uyama and Kobayashi, 1994), where the leaving vinyl alcohol tautomerizes to acetaldehyde, and hence the polymerization proceeds irreversibly. Lipase derived from *Pseudomonas fluorescens* (lipase PF) is effective for the polymerization. Bis(2,3-butanedione monoxime) alkanedioates are used as new diester monomer for the enzymatic synthesis of polyesters (Athawale and Gaonkar, 1994). This monomer is polymerized with glycols under mild reaction conditions (30 °C).

Unsaturated ester oligomers have been synthesized by the lipase-catalyzed polymerization of diesters of fumaric acid and 1,4-butanediol (Geresh and Gilboa, 1990). Isomerization of the double bond does not



Scheme 16-7.

occur to give all-trans oligomers showing crystallinity, whereas the industrial, unsaturated polyester having a mixture of cis and trans double bonds is amorphous (Geresh et al., 1993). The enzymatic polymerization of bis(2-chloroethyl) fumarate with xylylene glycol produces the unsaturated oligoester containing aromaticity in its backbone (Geresh and Gilboa, 1991). An all-cis unsaturated polymer is synthesized from dimethyl maleate with 1,6-hexanediol using *Candida antartica* lipase (lipase CA) immobilized on a macroporous resin (Mezoul et al., 1995 b, 1996 a).

Aromatic polyesters are synthesized from methyl terephthalate or isophthalate with 1,6-hexanediol in the presence of lipase CA (Mezoul et al., 1996 b). In using methyl isophthalate as monomer, macrocyclic compounds are formed as a by-product. Protease is also effective as a catalyst for polyester synthesis: *Bacillus licheniformis* protease catalyzes the oligomerization of esters of terephthalic acid and 1,4-butanediol (Park et al., 1994).

The PPL-catalyzed polymerization of bis(2,2,2-trichloroethyl) *trans*-3,4-epoxyadipate with 1,4-butanediol proceeds enantiospecifically to give an optically pure polyester (Scheme 16-7) (Wallace and Morrow, 1989 b). The (-) polymer with enantiopurity of 96% is obtained by adjustment of the monomer molar ratio between the di-

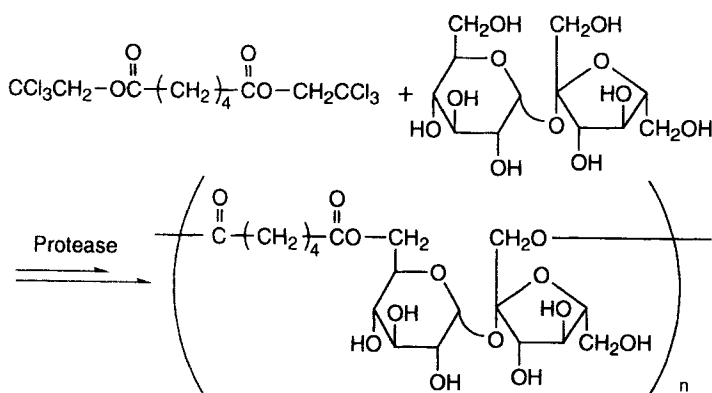
ester and the diol to 2:1. Optically active trimer and pentamer are prepared from racemic bis(2-chloroethyl) 2,5-dibromoadipate with 1,6-hexanediol using *Aspergillus niger* lipase as the catalyst (Margolin et al., 1987).

Lipase CA induces the regioselective oligocondensation of cholic acid in the 3-position (Noll and Ritter, 1996). A polyester containing a sugar group in the backbone is synthesized by protease-catalyzed polymerization of sucrose with bis(2,2,2-trichloroethyl) adipate, in which the hydroxyl group at the C6 and C1' positions of the sucrose is regioselectively reacted (Scheme 16-8) (Patil et al., 1991).

The enzymatic oligomerization of 12-hydroxyauric acid using lipase CA catalyst in the presence of 11-methacryloylaminoundecanoic acid produces a methacryl-type macromonomer (Noll and Ritter, 1997).

A new type of enzymatic polymerization, ring-opening poly(addition-condensation) of cyclic acid anhydrides with glycols has been reported (Kobayashi and Uyama, 1993). The polymerization of succinic anhydride with 1,8-octanediol using lipase PF proceeds at room temperature.

Lactones of different ring size are subjected to lipase-catalyzed, ring-opening polymerizations, yielding the corresponding polymers. So far, small-size (four-membered) and medium-size (six- and seven-



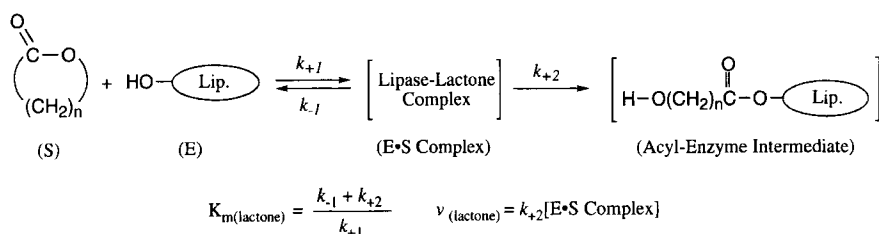
Scheme 16-8.

membered) lactones, as well as macrolides (12, 13, and 16-membered), have been reported to be polymerized through lipase catalysis. As for the four-membered lactones, lipase induces the polymerization of  $\beta$ -butyrolactone (Nobes et al., 1996),  $\alpha$ -methyl- $\beta$ -propiolactone (Svirkin et al., 1996),  $\beta$ -propiolactone (Namekawa et al., 1996), and benzyl  $\beta$ -malolactone (Matsumura et al., 1996). In using  $\alpha$ -methyl- $\beta$ -propiolactone, the polymerization proceeds enantioselectively to produce an optically active polymer. Polymerization of the medium-size lactones,  $\delta$ -valerolactone ( $\delta$ -VL, six-membered) and  $\epsilon$ -caprolactone ( $\epsilon$ -CL, seven-membered), occurs using lipase catalyst in bulk (Uyama and Kobayashi, 1993) or in organic solvents (Knani et al., 1993; MacDonald et al., 1995; Henderson et al., 1996). The polymerization behavior greatly depends on the reaction conditions and the enzyme origin. The copolymerization of lactones takes place via lipase catalysis. Random copolymers are obtained from  $\epsilon$ -CL and  $\delta$ -VL using lipase PF catalyst (Uyama et al., 1993).

Lipase catalyzes the ring-opening polymerization of macrocyclic esters, 11-undecanolide (12-membered) (Uyama et al., 1995 a), 12-dodecanolide (DDL, 13-membered) (Uyama et al., 1995 b), and 15-pentadecanolide (PDL, 16-membered) (Uyama

et al., 1996 a). Lipase CC is a suitable catalyst for the preparation of the high molecular mass polyester from the macrolide. Polymerization using *Pseudomonas* family lipase proceeds faster than with other types of the enzyme (Uyama and Kobayashi, 1996).

Macrolides have virtually no ring strain, and hence show similar reactivities with acyclic fatty acid alkyl esters in the alkaline hydrolysis and lower anionic ring-opening polymerizability than  $\epsilon$ -CL. On the other hand, the macrolides show unusual reactivity in the lipase catalysis, where their polymerization proceeds much faster than with  $\epsilon$ -CL. The difference in the enzymatic polymerizability has been quantitatively evaluated according to Michaelis–Menten kinetics (Scheme 16-9) (Uyama et al., 1997 a). Table 16-1 shows the kinetic parameters,  $K_{\text{m(lactone)}}$  and  $V_{\text{max(lactone)}}$ . The reciprocal values of  $K_{\text{m(lactone)}}$  of the lactones are close to each other and  $V_{\text{max(lactone)}}$  increases as the ring size becomes larger, indicating that the larger polymerizability of the macrolides through lipase catalysis is mainly due to the larger reaction rate ( $V_{\text{max}}$ ), but not to the binding abilities. These results suggest that the reaction process from the lipase–lactone complex to the acyl–enzyme intermediate is the key step for the polymerization.



Scheme 16-9.

**Table 16-1.** Michaelis–Menten kinetic parameters in the ring-opening polymerization of lactones catalyzed by lipase PF<sup>a</sup>.

Lactone	$K_{m(\text{lactone})}$ (mol l <sup>-1</sup> )	$V_{\text{max}(\text{lactone})}$ ( $\times 10^2$ , mol l <sup>-1</sup> h <sup>-1</sup> )
$\epsilon$ -CL	0.61	0.66
DDL	1.1	2.3
PDL	0.80	6.5

<sup>a</sup> Polymerization was carried out using lipase PF catalyst in the presence of 1-octanol (0.03 M), in *i*-propyl ether (10 ml) at 60 °C.

Polyester macromonomers are enzymatically synthesized in a single step procedure. The lipase PF-catalyzed polymerization of DDL in the presence of vinyl methacrylate produces a methacryl-type polyDDL macromonomer (Uyama et al., 1995 c). This process can be applied to the synthesis of telechelics having carboxylic acid groups at both ends by polymerization in the presence of divinyl sebacate.

Lipase PF is immobilized on a Celite and used for the enzymatic polymerization of DDL (Uyama et al., 1996 b). The immobilized enzyme prepared in the presence of sugars shows much higher catalytic activity than the native lipase. The turnover of this immobilized lipase is more than  $1 \times 10^4$ .

Enzymes can also be used as catalysts for the modification of polymers. The enzymatic transesterification of amylose film with vinyl caprate in the isooctane solution con-

taining solubilized subtilisin Carlsberg produces an amylose derivative regioselectively acylated at the C6 position (Bruno et al., 1995 a).

Lipase CA catalyzes the ring-opening polymerization of a six-membered cyclic carbonate, 1,3-dioxo-2-one, yielding poly(trimethylene carbonate) (Kobayashi et al., 1997 b). During the polymerization, decarboxylation does not take place. Oligocarbonate is enzymatically synthesized by the polymerization of carbonic acid diphenyl ester with bisphenol-A using lipase CC in an aqueous acetone (Abramowicz and Keese, 1989).

Cellulase is used as a dehydrating catalyst for the synthesis of polyesters and polyamides. The enzymatic polymerization of chiral fluorinated materials having two functional groups (OH or NH<sub>2</sub> and COOH) in the molecule using modified cellulase catalyst produces chiral polyesters or polyamides of narrow molecular weight distribution (Kitazume et al., 1988).

### 16.3.4 Polyaromatics

In living cells, various oxidoreductases play an important role in maintaining the metabolism of living systems. So far, several oxidoreductases, peroxidase, laccase, bilirubin oxidase, etc., have been reported to catalyze the oxidation polymerization of phenol and aniline derivatives, yielding polyaromatics.



Peroxidase catalyzes the decomposition of hydrogen peroxide at the expense of aromatic proton donors, typically phenol and aniline derivatives, in living cells. The peroxidase-catalyzed oxidation of these donors proceeds fast in an aqueous media, in some cases yielding water-insoluble oligomeric materials. The low solubility of the oligomer towards water prevents the formation of high molecular weight polymers.

Horseradish peroxidase (HRP) polymerizes *p*-phenylphenol in a mixture of water and water-miscible solvents such as 1,4-dioxane, acetone, *N,N*-dimethylformamide (DMF), and methyl formate to produce novel polyaromatics (Dordick et al., 1987). The reaction medium's composition greatly affects the molecular weight and 85% 1,4-dioxane affords the highest molecular weight ( $2.6 \times 10^4$ ). The structure of the resulting polymer is very complicated; the polymer is mainly of *ortho-ortho* linkage (Akkara et al., 1991).

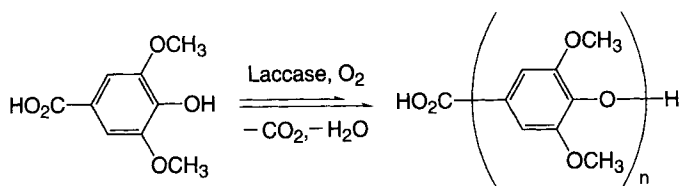
Various phenol derivatives are also polymerized through HRP catalysis in the aqueous organic solvent. The HRP-catalyzed polymerization of phenol in a mixture of 1,4-dioxane and phosphate buffer (pH 7) (80:20 vol.%) gives polymeric materials (Uyama et al., 1994 a, 1996 c). The polymer is partly soluble in DMF and dimethyl sulfoxide (DMSO), but insoluble in water, acetone, methanol, and benzene. The molecular weight of the DMF soluble part is  $3.5 \times 10^4$ . NMR and IR analyses show that the polymer is mainly a mixture of phenylene and oxyphenylene units. The polymer is relatively thermally stable. The temperature at 10 wt.% loss under air is 387 °C. The polymer completely decomposes around 571 °C under air and 43% remains at 1000 °C under nitrogen. The residue is supposed to be a carbonized polymer such as polyacene and graphite. DSC analysis of the polymer shows no clear glass transition tem-

perature ( $T_g$ ) and melting point ( $T_m$ ). Soybean peroxidase (SBP) also catalyzes the polymerization of phenol in the aqueous organic solvent (Uyama et al., 1995 d). The resulting polymer shows similar properties to those obtained by using an HRP catalyst.

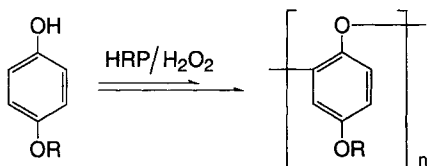
The HRP-catalyzed polymerization of alkylphenols in a mixture of phosphate buffer and 1,4-dioxane has been examined (Kurioka et al., 1994; Uyama et al., 1997 b). The polymerization behavior depends on the position and structure of the substituent. In the case of *p-n*-alkylphenols, the polymer yield increases on increasing the alkyl chain length from 1 to 5. Polymeric materials are obtained from all the cresol isomers by HRP and SBP catalysts (Uyama et al., 1995 e). The polymer can be obtained in a high yield from *p-i*-propylphenol, whereas the *o*- and *m*-isomers are not polymerized under similar reaction conditions. The polymer prepared in the aqueous, 1,4-dioxane shows low solubility towards common organic solvents, and the molecular weight is in the range of several thousand. On the other hand, soluble oligomers with molecular weights less than 1000 are formed using an aqueous DMF as the solvent (Ayyagari et al., 1995). Most of the enzymatically synthesized poly(alkylphenol)s possess no clear  $T_g$  and  $T_m$ . The cured polymer from *p-t*-butylphenol has  $T_g$  and  $T_m$  at 182 and 233 °C, respectively.

Peroxidases (HRP and SBP) and laccase induce the oxidative polymerization of 2,6-dimethylphenol in a mixture of acetone and acetate buffer (pH 5) (50:50 vol.%) to produce soluble poly(2,6-dimethyl-1,4-oxyphenylene) with a molecular weight of several thousand. This polymer with a higher molecular weight is widely used for high performance engineering plastics showing high thermostability (Ikeda et al., 1996 a).

4-Hydroxybenzoic acid derivatives, 3,5-dimethoxy-4-hydroxybenzoic acid (syrin-



Scheme 16-10.



Scheme 16-11.

gic acid), and 3,5-dimethyl-4-hydroxybenzoic acid are subjected to oxidative polymerization catalyzed by laccase or peroxidases. The polymerization of syringic acid using laccase derived from *Pycnoporus coccineus* proceeds at room temperature under air to produce poly(phenylene oxide) with a molecular weight up to  $1.8 \times 10^4$  (Scheme 16-10) (Ikeda et al., 1996b). The polymerization is a new type of enzymatic polymerization involving the elimination of carbon dioxide and hydrogen from the monomer.

HRP catalyzes the polymerization of *p*-alkoxyphenols in the aqueous organic solvent to produce polymer showing high solubility towards polar organic solvents such as chloroform, acetone, and DMF (Scheme 16-11) (Kurioka et al., 1996). In the IR chart of the polymer, there is almost no absorbance due to O–H vibration, indicating the regioselective synthesis of a novel poly(phenylene oxide) through the enzyme catalysis.

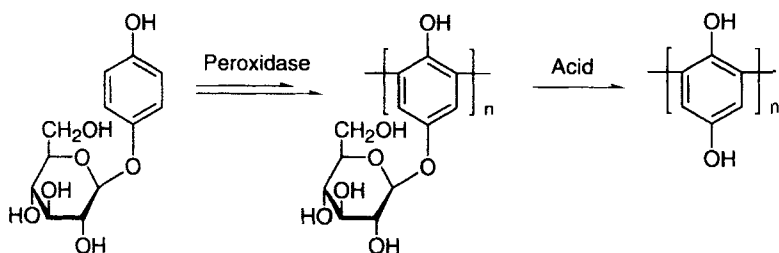
The HRP-catalyzed polymerization of 4,4'-biphenol in a mixture of 1,4-dioxane and phosphate buffer (pH 7) (80:20 vol.%) affords polymer that is soluble in polar organic solvents (Kobayashi et al., 1996d).

The molecular weight and its distribution of the methylated polymer are  $7.3 \times 10^3$  and 6.8, respectively. The larger molecular weight distribution value is probably because the polymer contains branching structures. 2,2-Bis(4-hydroxyphenyl)propane (bisphenol-A), and bis(4-hydroxyphenyl) ether are also enzymatically polymerized.

The mechanistic study of HRP-catalyzed oxidative polymerization is performed using NMR spectroscopy (Alva et al., 1997). In the initial stage of the polymerization of 8-hydroxyquinoline-5-sulfonate, the 2, 4, and 7-positions of the monomer are involved in the radical coupling.

Bilirubin oxidase (BOD), a copper-containing oxidoreductase, catalyzes the oxidative polymerization of 1,5-dihydroxynaphthalene (Wang et al., 1993). A mixed solvent of 1,4-dioxane, ethyl acetate, and acetate buffer (pH 5.5) affords a polymer that is barely soluble in common organic solvents. The polymerization proceeds regioselectively to produce the polymer film having a long  $\pi$ -conjugated structure.

Glucose  $\beta$ -D-hydroquinone (arbutin) can be polymerized by HRP and SBP in a buffer to produce a water-soluble polymer with molecular weight ranging from 1600 to 3200 (Wang et al., 1995). Treatment of the polymer with 5 M HCl leads to quantitative deglycosylation of the polymer, yielding poly(hydroquinone) soluble in THF, DMSO, DMF, acetone, and methanol. NMR analysis of the polymer shows that the polymer is of *ortho-ortho* coupling structure (Scheme 16-12), which is different from that prepared electrochemically.



Scheme 16-12.

Lignin monomers, *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol are oxidized by the HRP catalyst. In vitro lignin synthesis has been performed by the HRP-catalyzed terpolymerization of them (14:80:6 mol%) in an extremely dilute aqueous solution at pH 5.5 (Freudenberg, 1965). The dialysis membrane method is applied to the polymerization of coniferyl and sinapyl alcohols, yielding insoluble polymeric materials (Tanahashi and Higuchi, 1981). Using a mixture of acetone and buffer (pH 7) (20:80 vol.%) as solvent improves the polymer yield (Okusa et al., 1996).

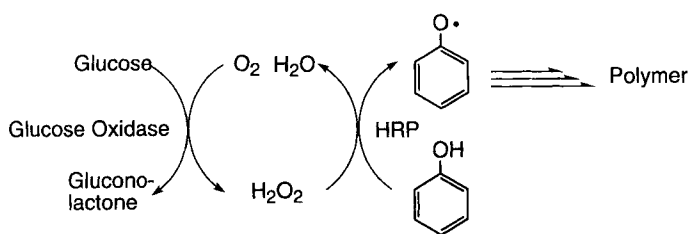
Laccase is also known to catalyze the dehydrogenative polymerization of coniferyl alcohol (Hüttermann et al., 1980). The polymer formation is dependent on the enzyme's origin (Okusa et al., 1996). The polymerization, catalyzed by laccase from *Pycnoporus coccineus* in the equivolume mixture of acetone and buffer (pH 7), gives the polymer quantitatively. The polymer yield is low on using *Coriolus versicolor* laccase as the catalyst. Laccase from *Rhus vernicifera* Stokes does not induce the polymerization.

The grafting of polyphenols on lignin has been attempted by the HRP-catalyzed polymerization of *p*-cresol in the presence of lignin (Popp et al., 1991; Blinkovsky and Dordick, 1993). The phenolic moiety of the lignin is reacted with *p*-cresol in the aqueous 1,4-dioxane. The product is highly insoluble in DMF, suggesting crosslinking of lignin via polyphenol bridges.

The enzymatic polymerization of coal has been examined in a mixture of DMF and buffer (Blinkovsky et al., 1994). HRP and SBP can catalyze the oxidative polymerization of the low molecular weight coal polymer (4 kDa). The resulting product is partly soluble in DMF, and the DMF-soluble part has a larger molecular weight than that of the starting coal.

The bienzymatic system (glucose oxidase + HRP) is used as the catalyst for polyphenol synthesis. This system induces the polymerization of phenol in the presence of glucose, without the addition of hydrogen peroxide, to produce the polymer in a moderate yield (Uyama et al., 1997c). Hydrogen peroxide is formed in situ by the oxidation of glucose catalyzed by glucose oxidase, which is used as an oxidizing agent for the polymerization (Scheme 16-13).

Polymer precipitates are often formed during the enzymatic polymerization of phenol derivatives in an aqueous organic solvent. By the addition of hydrophilic (water-soluble) polymers into the reaction mixture, the precipitate is stabilized to form polymeric microspheres (dispersion polymerization). The HRP-catalyzed polymerization of phenol in the presence of poly(vinyl methyl ether) (PVME) in 1,4-dioxane-phosphate buffer (60:40 vol.%) affords relatively monodisperse particles of sub-micrometer size (Uyama et al., 1995f). The particle size is controlled by the concentration of PVME and the solvent composition.



Scheme 16-13.

Enzymatic oxidations can be applied to the hardening of phenol derivatives. Cross-linked polymeric materials are obtained from catechol derivatives bearing an unsaturated alkenyl group at the 4-position of the catechol ring using *Pycnoporus* laccase (Teraada et al., 1994). The monomer having the *cis*-9,12,15-octadecatrienyl or *cis*-9,12-octadecadienyl group in the side chain affords polymeric film showing ideal dynamic viscoelasticity.

Three interfacial systems, reverse micelles, Langmuir trough, and a biphasic system, have been examined for the enzymatic synthesis of polyaromatics. HRP and *p*-ethylphenol are encapsulated in the reverse micelle, which is a ternary system composed of isooctane, water, and bis(2-ethylhexyl) sodium sulfosuccinate (AOT). The introduction of hydrogen peroxide into the system induces the polymerization to produce the polymer quantitatively (Rao et al., 1993). This system affords the spherical polymer particles in the diameter range from 0.1 to 2  $\mu\text{m}$  (Akkara et al., 1994a). Cresols are polymerized in the reverse micellar system using HRP or SBP catalyst (Uyama et al., 1995e). This system can be applied to the synthesis of a fluorescent polymer from 2-naphthol using an HRP catalyst (Premachandran et al., 1996).

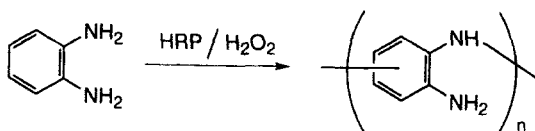
The enzymatic polymerization of phenol derivatives of a monolayer form has been examined. A mixture of *p*-tetradecyloxyphenol and phenol formed a monolayer at the air–water interface in a Langmuir trough

and was polymerized by an HRP catalyst in the subphase (Bruno et al., 1995b, c). The film can be deposited on a silicon wafer with a transfer ratio of 100% for the Y-type film. Eppipsometric and AFM analyses show a monolayer thickness of 27.8 Å (2.78 nm).

The HRP-catalyzed polymerization of *p*-alkylphenols has been examined in a biphasic system consisting of two mutually immiscible phases (isooctane and water) (Ayyagari et al., 1996). The alkyl chain length of the monomer and the solvent composition affect the polymerization behavior.

Tyrosinase can be used as a catalyst for the modification of chitosan. The enzymatic treatment of chitosan film in the presence of tyrosinase and phenol derivatives produces a new material of chitosan derivative (Payne et al., 1996). During the reaction, unstable *o*-quinones are formed, followed by the reaction with chitosan to give the modified chitosan.

Oxidoreductases can catalyze the oxidative polymerization of aromatic amines. HRP and BOD induce the polymerization of aniline. HRP produces a polyaniline consisting of at least two units (Akkara et al., 1992). One is composed of an alternating benzoid–quinoid structure, which is the same as the chemically obtained polymer structure. The others consist of *ortho*- and *para*-substituted carbon–carbon and carbon–nitrogen bond structures. Polymerization in the presence of a BOD-adsorbed solid matrix gives a polyaniline film contain-



Scheme 16-14.

ing the active enzyme (Aizawa et al., 1990). The polymer is mainly of a 1,4-substitution structure. The film is electrochemically reversible in its redox properties in acidic solution.

The HRP-catalyzed oxidative polymerization of *o*-phenylenediamine in a mixture of 1,4-dioxane and phosphate buffer produces a soluble polymer with a molecular weight of  $2 \times 10^4$  (Kobayashi et al., 1992 c). The resulting polymer has an iminophenylene unit (Scheme 16-14), which is not usually obtained by conventional oxidative polymerization. Polymers can be enzymatically obtained from various aniline derivatives such as 4-substituted *o*-phenylenediamines, *p*-phenylenediamine, *p*-aminophenylmethylcarbitol, *p*-aminobenzoic acid, and *o*- and *p*-aminophenols (Kobayashi et al., 1994 a; Alva et al., 1996; Arias-Marín et al., 1996).

Polyaniline monolayers can be obtained by the formation of monolayers of an aniline/*p*-hexadecylaniline mixture by the LB technique at the air–water interface, followed by oxidative polymerization using an HRP catalyst (Akkara et al., 1994 b; Bruno et al., 1995 b, c).

The HRP-catalyzed oxidative copolymerization of phenol with *o*-phenylenediamine is performed in an aqueous organic solvent (Uyama et al., 1994 b). The copolymer is partly soluble in DMF, and the molecular weight of the soluble part is about  $5 \times 10^3$ . IR analysis shows that the structure of the copolymer is a mixture of the units obtained by the homo-polymerization of both monomers.

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## 17 Biosynthetic Routes to Novel Macromolecular Materials

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## List of Symbols and Abbreviations

$a, b, c$	unit cell spacing
$A_p$	mole fraction styrene
$K_m$	Michaelis constant
$k_{cat}$	turnover number
$m$	mass
$V$	reaction rate
$W_x$	weight fraction
$X$	degree of polymerization
$X_n$	number average degree of polymerization
$z$	charge
Ala	alanyl
Arg	arginyl
Asp	aspartyl
AUG	adenine uracil guanine
Aze	azetidinecarboxylic acid
CGA	cytosine guanine adenine
CP/MAS	cross-polarization/magic angle spinning
Dhp	dehydroproline
DNA	deoxyribonucleic acid
DSC	differential scanning calorimetry
FTIR	Fourier transform infrared spectroscopy
GCU	guanine cytosine uracil
Glu	glutamyl
Gly	glycyl
HAP	hybrid artificial protein
HEPES	<i>N</i> -(2-hydroxyethyl)piperazine- <i>N'</i> -2-ethanesulfonic acid
IR	infrared
Leu	leucyl
MAS	magic angle spinning
Met	methionyl
mRNA	messenger ribonucleic acid
NMR	nuclear magnetic resonance
PBLG	poly( $\gamma$ -benzyl- $\alpha$ ,L-glutamate)
PfF	<i>p</i> -fluorophenylalanine
Phe	phenylalanyl
PLGA	poly( $\alpha$ ,L-glutamic acid)
PMMA	poly(methylmethacrylate)
Pro	prolyl
PTE	phosphotriesterase
RNA	ribonucleic acid
SDS-PAGE	sodium dodecyl sulfate–polyacrylamide gel electrophoresis
SeMet	selenomethionine

3TA	3-thienylalanine
tfL	trifluoroleucine
tRNA	transfer ribonucleic acid
UV	ultraviolet
WAXD	wide angle X-ray diffraction

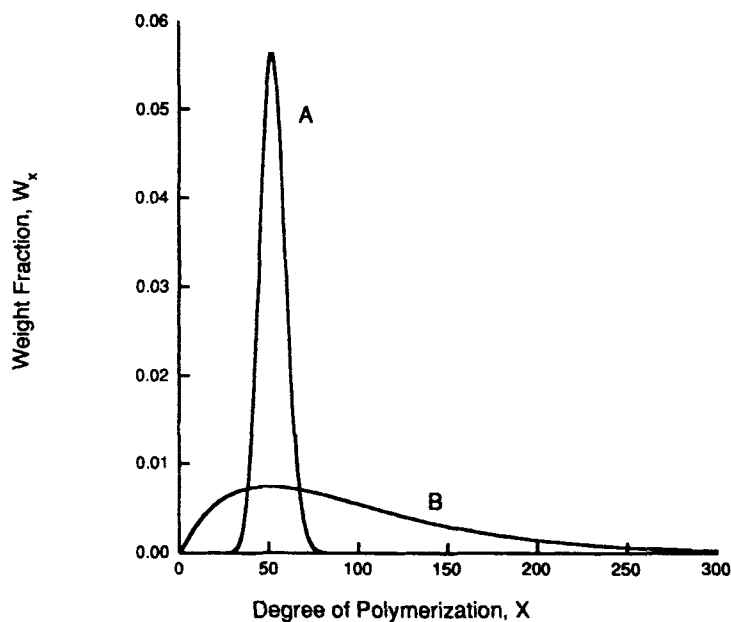
## 17.1 Introduction

The ability to control the properties of macromolecular materials lies in the ability to control four critical aspects of polymer microstructure: molecular weight, stereochemistry, composition, and sequence. A primary focus of polymer synthetic research for decades has been the development of polymerization processes that permit increasingly precise control of chain architecture. In recent years, our laboratory has investigated *in vivo* protein synthesis as a method for producing novel macromolecular materials in which nearly absolute control over all aspects of polymer structure is afforded. Applications for these unique materials include those involving processes that occur on the nanometer length scale and in which absolute control over macromolecular structure and surface chemistry are important, such as the formation of nanostructures and molecular recognition.

Advances in traditional polymer synthesis methods (such as living and Ziegler–Natta polymerizations) have been critical in de-

veloping our understanding of macromolecular structure–property relationships and in producing polymeric materials that are useful as plastics, fibers, and elastomers. These methods are limited, however, in producing materials with architectures and surface chemistries precisely controlled on the nanometer length scale, because the nature of chemical polymerization process requires that the resulting polymers exist as a mixture of products and not as collections of identical macromolecules.

Living polymerizations (Szwarc et al., 1956; Szwarc, 1956, 1968; Waack et al., 1957; Puskas et al., 1982–83; Faust et al., 1982–83, 1989; Faust and Kennedy, 1986; Schrock, 1990), developed by Szwarc and co-workers in the 1950s, have enabled the polymer chemist to achieve the highest possible molecular weight homogeneity for any linear polymerization and to produce a wide variety of topologies, such as telechelic macromonomers and block, star, and comb copolymers. The ability to produce a nearly monodisperse Poisson molecular weight distribution (Fig. 17-1) represents a pro-

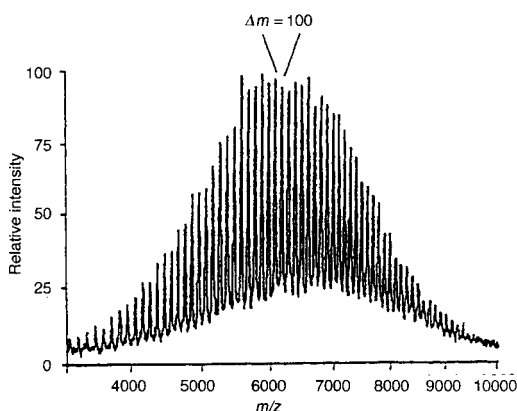


**Figure 17-1.** Comparison of the weight fraction distributions for A, the Poisson distribution, and B, the most probable distribution (Flory) of a polymer with an average  $X_n$  of 50.

found advance over the control afforded by simple step and chain growth polymerizations. Monodispersity in this sense, however, does not correspond to the existence of a single molecular weight species. Indeed, a poly(methyl methacrylate) sample with a molecular weight distribution of 1.03, among the lowest practically achievable with living polymerization methods, consists of a strikingly heterogeneous distribution of chain lengths, as shown in Fig. 17-2. In addition, the pool of monomers amenable to living polymerizations is limited largely to nonpolar monomers, with the exception of the living anionic polymerization of methacrylate monomers (Teyssie et al., 1990; Granel et al., 1997).

Ziegler–Natta polymerization of  $\alpha$ -olefins (Corradini, 1995; Pino and Moretti, 1987), another significant synthetic development of the 1950s, offers superb control of the stereochemistry and structure of polyolefin chains, yielding polymers of high molecular weight with nearly perfect control of tacticity and branching. The stereochemical control offered by these and other organometallic catalysts (Brintzinger et al., 1995) has yielded a variety of useful thermoplastic polymers and elastomers. There are, however, only a limited number of nonpolar monomers that can be used with these catalysts, and limited control of the molecular weight is achieved, with polydispersities commonly on the order of 5–30 (Odián, 1991).

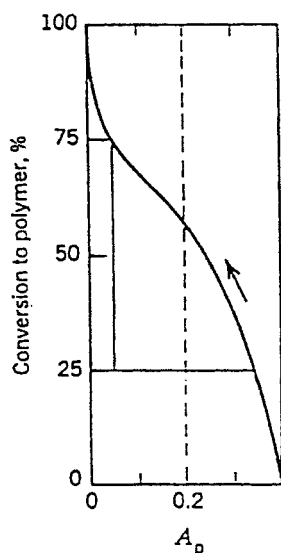
Copolymerization methods have also had enormous commercial importance, due their ability to combine the properties of two or more distinct monomers into a single chain. A wide range of novel bulk and interfacial properties has been accessed as a result of these developments. Control of molecular weight and stereochemistry, however, is subject to the limitations of conventional step and chain growth polymerizations, and



**Figure 17-2.** Matrix-assisted laser desorption mass spectrum of an approximately 6500 molecular weight poly(methyl methacrylate) with a polydispersity index of 1.03. [Reproduced with permission from Bahr et al. (1992).]

even the control of composition and sequence of the copolymer chain is restricted. The compositional drift encountered in nearly all copolymerizations results in a range of compositions for any given copolymerization, which has critical effects on the chemical and physical properties of the copolymer product. An example of this phenomenon is shown in Fig. 17-3 for the copolymerization of styrene and methyl acrylate (Skeist, 1946); the drastic change in copolymer composition as the conversion advances results in a brittle and opalescent material due to the incompatibility of the various components of the polymer mixture. Furthermore, even in cases in which compositional drift is absent (Bartlett and Nozaki, 1946) and the polymer length is fixed, there is no control over the sequence of monomers in the copolymer chain, and the copolymer mixture exists as a large number of isomers with different monomer sequences which can be predicted by statistical models (Tirrell, 1986; Wall, 1941).

Template polymerization has also been investigated as a method to improve control over polymer properties (Tan, 1994; Ander-

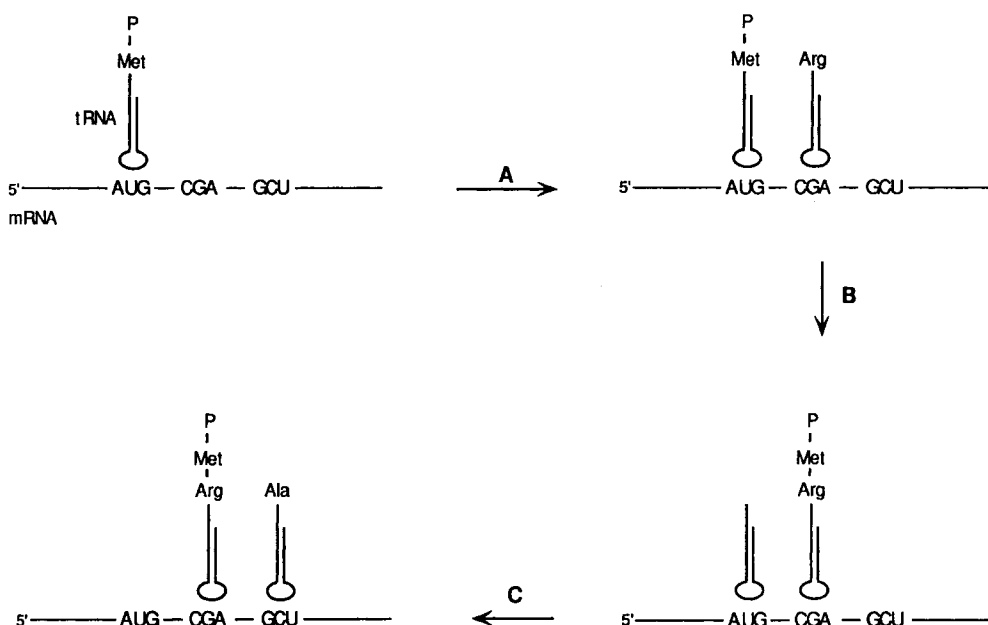


**Figure 17-3.** Copolymer composition ( $A_p$  = mole fraction styrene) in the copolymerization of styrene and methyl acrylate prepared from an initial monomer feed containing 0.2 mole fraction styrene, plotted as conversion vs. instantaneous copolymer composition. [Reproduced with permission from Skeist (1946).]

son et al., 1993). In theory, this method permits many copies of a target daughter polymer to be produced from a parent template with increased control over the propagation rate, molar mass, and microstructure. In practice, the presence of a template has been shown to significantly influence polymerization variables in only a limited number of cases (Baranovsky et al., 1992; Gons et al., 1975). Additionally, the degree of polymerization of the daughter polymer is only very rarely matched to that of the template, and separation of the daughter from the template is complicated. Copolymers are seldom used as templates owing to difficulties in controlling polymer association, which limits the utility of the method in controlling monomer sequence. Furthermore, control of the daughter polymer's properties is limited by the same statistical considerations, given above, which govern the properties of the parent polymer.

While the statistical nature of conventional polymer products has not limited their use in many applications, their relevance to applications in which the size and chemical nature of individual macromolecules becomes important has been severely restricted. With increasing technological interest in forming well-defined architectures and surface chemistries for nanostructures, biomaterials, and biosensor applications (Hubbell, 1995; Langer, 1995; Ratner, 1993; Hodges, 1996; Takeuchi and Matsui, 1996; Mosbach and Ramstrom, 1996), the need to synthesize precisely engineered macromolecules has gained new importance. To this end, materials scientists have looked to Nature's precise control over macromolecular structure and function as a model for producing materials. Nature is an appropriate model system for exerting this level of control, since some natural polymers (specifically proteins and nucleic acids) exhibit uniform and precise molecular weights, stereochemistries, compositions, and sequences, which are critical to their function in self-assembly and molecular recognition.

Protein synthesis *in vivo* is a template-directed polymerization in which messenger RNA (mRNA) directly encodes cellular DNA information. At the ribosome, mRNA is read by transfer RNA (tRNA) to convert the coding sequence into a corresponding sequence of amino acids linked together enzymatically to form the protein (Fig. 17-4). Because the tRNA is charged with the appropriate amino acid by a highly selective aminoacyl-tRNA synthetase, the error frequency in amino acid incorporation is very small (ca.  $1$  in  $10^4$ ) (Parker, 1989). Given the ability to design and construct DNA sequences and incorporate them into cellular hosts via recombinant methods, the use of *in vivo* protein synthesis has become an attractive technique for producing unique protein polymers in which all aspects of the



**Figure 17-4.** Schematic representation of the template nature of in vivo protein synthesis (P designates the protein chain). A) An aminoacyl-tRNA (Arg in this example) is delivered to the ribosome and binds through its anticodon to the mRNA. B) Peptide bond formation is catalyzed by peptidyl transferase. C) The ribosome moves down the mRNA chain, and the next aminoacyl-tRNA is delivered to the ribosome.

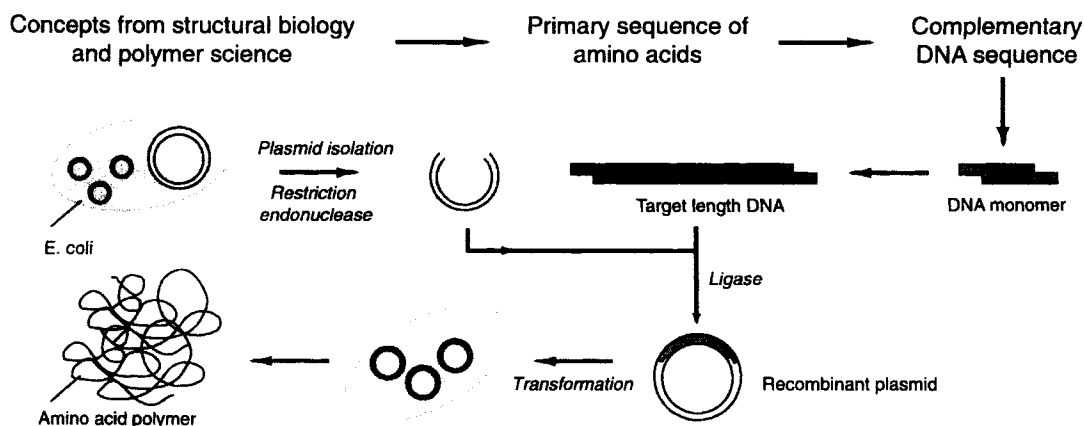
polymer microstructure are controlled simultaneously. This level of control permits engineering not only of the structures the materials can assume, but also of the functions the materials can perform.

In addition to the synthetic advantages afforded by in vivo protein synthesis, there are several advantages in using proteins as materials. While the utility of proteins in materials applications requiring high temperature or solvent resistance is limited, proteins have many useful materials properties, as evidenced by nature's use of these polymers in hair, skin, and bone. Proteins assume well-ordered, thermodynamically stable, three-dimensional conformations in both the solid and solution states, and are therefore capable of spontaneous self-assembly. The  $\alpha$ -helix, coiled-coil,  $\beta$ -sheet, and reverse turn structures adopted by proteins are critical in the catalytic function of many

globular proteins (e.g., lysozyme, glucose oxidase, and many others) and in the structural roles of fibrous proteins (e.g., collagen, keratin, elastin, silk). The incorporation of these structures into protein polymers ("artificial proteins") to control the three-dimensional structure may permit production of macromolecules with highly specialized functions as well as controlled biological activity and degradability. These properties are certain to play a significant role in the use of artificial proteins in biomaterials, biosensor, and nanostructure applications.

The importance of these structures in imparting useful materials properties has fueled interest in using recombinant methods to produce unique protein materials. Most often, recombinant methodologies are used for site-directed mutagenesis studies designed to probe the nature of protein fold-





**Figure 17-5.** Schematic diagram of gene construction and protein synthesis.

ing and enzymatic activity. As materials research has looked to nature for models of hierarchical structures, such as those found in collagenous tissues, however, the use of recombinant methods for the production of naturally occurring repetitive polypeptide sequences has increased. For example, silk (Capello et al., 1990), collagen (Goldberg and Salerno, 1990), elastin (McPherson et al., 1992), mussel adhesive proteins (Salerno and Goldberg, 1994; Filpula et al., 1990), viral proteins (O'Brien et al., 1994), and coiled-coil proteins (McGrath and Kaplan, 1993) have all been produced *in vivo* in order to produce the hierarchical structures common to these naturally occurring proteins.

In an effort to expand the repertoire of polymeric structures accessible via the recombinant approach, our laboratory has investigated the use of *de novo* ("from scratch") protein design (McGrath et al., 1992; Ferrari and Cappello, 1997) as a route to novel polymers which exhibit interesting and well-controlled materials properties. Amino acids exhibit distinct conformational and reactivity properties, which allow tailoring of the chemical, biological, and physical behavior of artificial proteins with a precision that is unattainable in conven-

tional polymeric materials. Although solid phase protein synthesis (Merrifield, 1978) can yield novel polypeptides with controlled sequences, the repetitive nature of the amino acid addition, coupled with the slightly less than quantitative yield in each step and lack of proofreading mechanisms, limits the practically achievable lengths to approximately 50 amino acid units. Oligopeptide repeats synthesized via solid phase methods can be linked chemically to form repetitive polypeptides (Nicol et al., 1994), but the length of the repeat is limited and the control over the product chain length is lost. A recombinant approach is therefore favorable, in that precise control of the amino acid sequence can be exercised in protein polymers of high molecular weight.

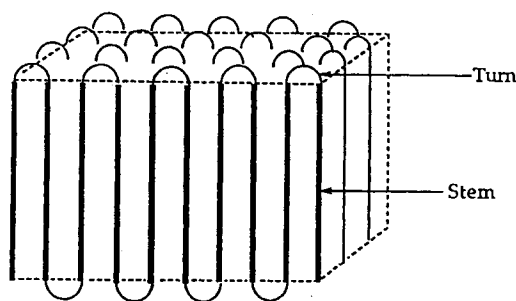
We have adopted the biosynthetic approach to protein polymer production summarized in Fig. 17-5. First, the target repeating unit sequence is identified based on consideration of its likely materials properties. An oligonucleotide which encodes the target repeating unit sequence is then synthesized via solid phase methods (McBride and Caruthers, 1983) and ligated (enzymatically) into a bacterial cloning vector. Following transformation of an appropriate bacterial strain, colonies are grown to per-

mit selection and amplification of the desired oligonucleotide. The integrity of the insert is verified via restriction analysis and standard sequencing methods (Sambrook et al., 1989), and the DNA is multimerized to form repetitive DNA sequences of varying molecular weights. The population of multimeric DNAs is again ligated into a cloning vector, and the desired multimer length is identified after amplification via bacterial growth. The target length DNA is inserted into an expression vector, which then contains the DNA sequence encoding the artificial protein of interest under the control of an appropriate promoter. This expression vector is used to transform an *E. coli* strain which has the necessary protein translational machinery. The bacterial host is then induced, via conventional molecular biological methods (Sambrook et al., 1989), to produce the artificial amino acid polymer, which is isolated and purified by appropriate protein purification protocols (Scopes, 1994).

These biosynthetic methods have proven useful in producing a series of protein polymers which exhibit well-defined structures, useful catalytic activity, and the capacity for molecular and cellular recognition. Novel protein materials produced in our laboratory are described below and include crystalline lamellar solids with controlled thickness and surface chemistry, liquid crystalline phases formed from helical rod-like polymers, catalytic surfaces with enzymatic activity, and repetitive protein polymers containing artificial amino acids.

## 17.2 Crystalline Lamellar Solids

The folded chain lamellar crystal is a well-known motif in polymer materials science, in that many flexible polymer chains adopt crystalline structures in which the

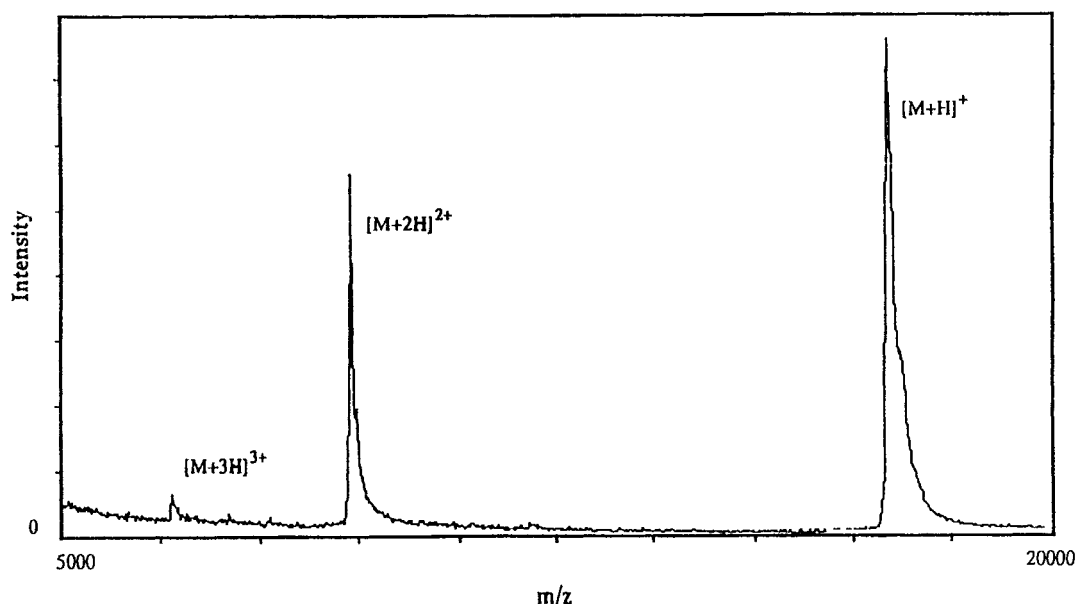


**Figure 17-6.** Schematic representation of a chain-folded lamellar crystal. [Reproduced with permission from Parkhe et al. (1993).]

chain runs perpendicular (or nearly perpendicular) to the lamellar surface and folds (more or less) regularly at that surface (Kelly, 1957). In synthetic polymers, the folded chain architecture is formed for kinetic reasons, i.e., the polymer chain is trapped in the folded geometry. Upon annealing, chain-folded lamellae increase in thickness as the chain approaches its thermodynamically stable, extended chain conformation. Because the thickness and surface chemistry of chain-folded lamellar crystals are not, in general, determined by thermodynamic factors, control of such properties has remained elusive.

Our initial attempts to design well-defined crystalline lamellar solids, such as the one shown schematically in Fig. 17-6, have been based on the knowledge that alanyl-glycine dyads form thermodynamically stable  $\beta$ -sheet structures in natural silk proteins (Fraser and McRae, 1973). Choice of the length of the  $\beta$ -sheet elements has been based on studies of aliphatic polyamides, which fold into crystalline lamellar solids with 6–8 lateral bonds per crystalline stem (Dreyfus and Keller, 1970; Atkins et al., 1992).

The selection of additional amino acids to promote folding in the structure reflected our initial expectation that proline and glutamic acid would be excluded from the la-



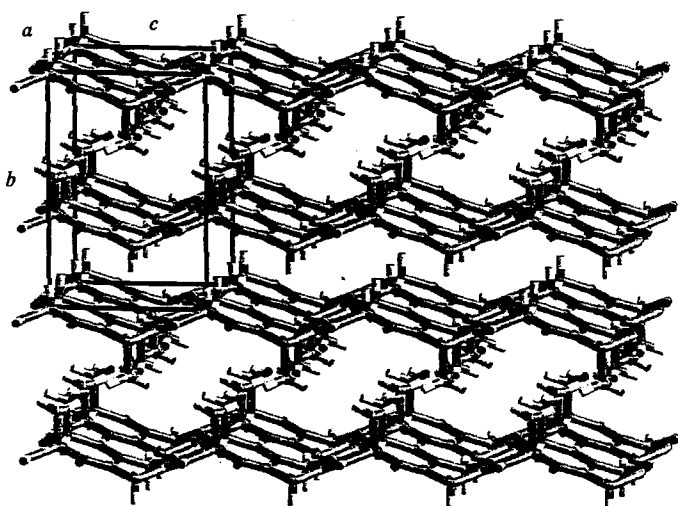
**Figure 17-7.** Matrix-assisted laser desorption mass spectrum of the repetitive polypeptide  $[(\text{AlaGly})_4\text{ProGluGly}]_{14}$ . Note the monodispersity of the sample relative to the PMMA sample shown in Fig. 17-2. [Reproduced with permission from Beavis et al. (1992).]

mellar interior of the crystal (Chou and Fasman, 1974). Proline frequently lies in  $\beta$ -turns in globular proteins (Chou and Fasman, 1974, 1977), and glutamic acid is the least likely of all amino acids to reside in a  $\beta$ -sheet (Chou and Fasman, 1974). Therefore the repetitive peptide sequences initially chosen for bacterial protein synthesis were  $[(\text{AlaGly})_n\text{ProGluGly}]_m$  (**1**) and  $[(\text{AlaGly})_n\text{GluGly}]_m$  (**2**), where  $n$  ranges from three to six and  $m$  from five to 54.

Bacterial expression of these repetitive peptides has been demonstrated (McGrath et al., 1992; Creel et al., 1991; Deguchi et al., 1994). Repetitive polymers of the nonapeptide  $(\text{AlaGly})_3\text{ProGluGly}$  have been produced from *E. coli* cultures transformed with a recombinant expression vector derived from pET-3b (Creel et al., 1991; Dunn and Studier, 1983; Studier et al., 1990); protein expression was monitored by *in vivo* incorporation of  $^3\text{H}$  glycine. Each of the target proteins accumulates in the cyto-

plasm of the bacterial cell and migrates as a single band in gel electrophoresis, indicating the absence of a broad distribution of molecular weights. Matrix-assisted laser desorption mass spectrometry corroborates these observations. Figure 17-7 shows the results for  $[(\text{AlaGly})_4\text{ProGluGly}]_{14}$ , which was obtained in a highly homogeneous form after dialysis to remove contaminating protein fragments (Creel et al., 1991).

In contrast to our expectations, wide angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), and Fourier transform infrared spectroscopy (FTIR) of the repetitive polymer **1** with  $n=3$  and  $m=54$  all indicate the formation of an amorphous glass rather than a  $\beta$ -sheet at room temperature (McGrath et al., 1992). Only diffuse halos are observed in WAXD, no crystalline melting endotherm is evidenced by DSC, and the infrared (FTIR) amide I and amide II bands are observed at 1653 and 1540  $\text{cm}^{-1}$ , respectively, rather than at ca.



**Figure 17-8.** Computer-generated representation of the solid state structure of  $[(\text{AlaGly})_3\text{GluGly}]_{36}$ . [Reproduced with permission from Krejchi et al. (1994).]

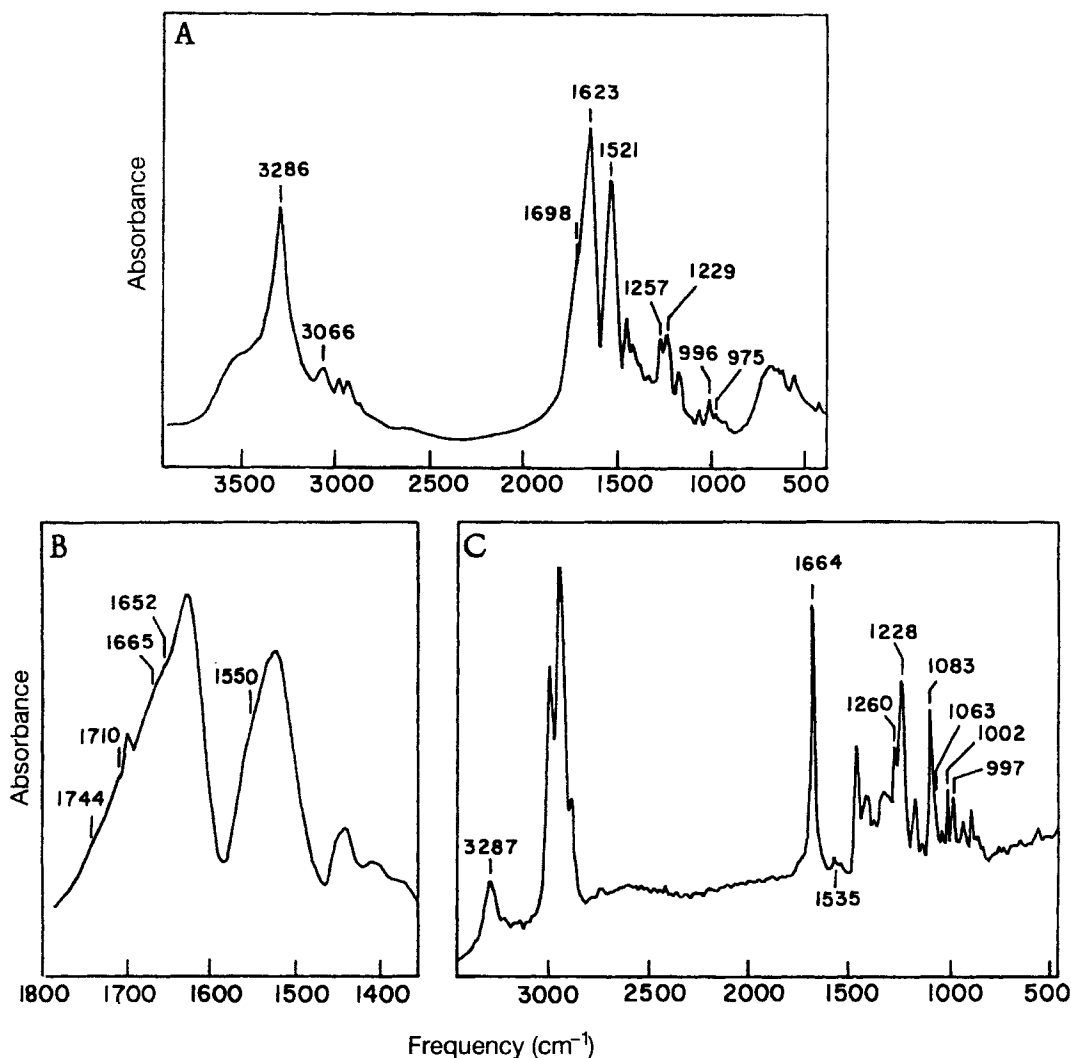
$1630$  and  $1525\text{ cm}^{-1}$ , as expected for a  $\beta$ -sheet polypeptide (Fraser et al., 1965; Moore and Krimm, 1968). It is likely that the steric bulk of the proline residue, coupled with the odd number of amino acids in the nonapeptide repeat, frustrates development of regularly folded, crystalline,  $\beta$ -sheet regions in this polymer.

Consistent with this hypothesis, bacterial expression and purification of polypeptide 2 with  $n=3$  and  $m=36$  produces a repetitive protein polymer which, when precipitated from 70% formic acid solution, forms a crystalline solid with primarily the  $\beta$ -sheet structure shown in Fig. 17-8 (Krejchi et al., 1994, 1996). As shown in Fig. 17-9 A, infrared spectroscopic analysis of the protein solid yields amide I, amide II, and amide III bands at  $1623$ ,  $1521$ , and  $1229\text{ cm}^{-1}$ , respectively, consistent with a  $\beta$ -sheet structure (Fraser et al., 1965; Moore and Krimm, 1968). In addition, the presence of a weak amide I band at  $1698\text{ cm}^{-1}$  is indicative of the antiparallel  $\beta$ -sheet architecture. The presence of the amide I component at  $1652\text{ cm}^{-1}$  and the shoulder at  $1665\text{ cm}^{-1}$  (Fig. 17-9 B) indicates that a fraction of the polypeptide does not adopt an antiparallel

$\beta$ -sheet arrangement. Figure 17-9 C shows the Raman amide I and amide III bands at  $1664$  and  $1260$  and  $1228\text{ cm}^{-1}$ , respectively, which are consistent with antiparallel  $\beta$ -sheet formation (Moore and Krimm, 1968; Frushour and Koenig, 1975). Furthermore cross polarization/magic angle spinning (CP/MAS)  $^{13}\text{C}$  NMR spectroscopy yields chemical shifts in good agreement with those observed for the  $\beta$ -sheet form of poly(L-alanylglycine).

Wide angle X-ray diffraction analysis of 2 yields discrete Bragg reflections indicating the crystalline nature of the protein polymer, with orthorhombic unit cell spacings ( $a=0.948\text{ nm}$ ,  $b=1.060\text{ nm}$ , and  $c=0.695\text{ nm}$ ), consistent with the hydrogen-bonding distance observed in many nylons and attributed to antiparallel  $\beta$ -sheet structures (Dreyfus and Keller, 1970; Keller, 1959; Atkins et al., 1972; Magill et al., 1981). It is worthwhile to note that the lamellar thickness is always shorter than the chain length in these polymers (Krejchi et al., 1994), as expected for the chain-folded lamellar architecture.

All of the above evidence indicates that a regular  $\beta$ -sheet structure is assumed by the



**Figure 17-9.** Vibrational spectra of polypeptide  $[(\text{AlaGly})_3\text{GluGly}]_{36}$ . A) Fourier transform infrared spectrum of a KBr pellet 0.2% in polypeptide. B) Expansion of the amide I region of the IR spectrum shown in A). C) Raman spectrum of the polypeptide. [Reproduced with permission from Krejchi et al. (1994).]

repetitive  $[(\text{AlaGly})_3\text{GluGly}]_{36}$  polypeptide upon crystallization. In such a folded-chain architecture, the periodic glutamic acid residues would be expected to decorate the lamellar crystal surface. Indeed, ionization of the glutamic acid residues by treatment of the polypeptide with dilute sodium methoxide-methanol solution does not result in any change in the chain conformation as assessed via vibrational spectroscopy, nor in

any changes in the intersheet packing distance as monitored by WAXD. These results suggest that the glutamic acid residues reside on the lamellar surface (Chen et al., 1995). More definitive evidence for the isolation of the glutamic acid residue on the surface of the lamellar crystal comes from MAS  $^{13}\text{C}$  NMR experiments on the related polymer  $[(\text{AlaGly})_3\text{GluGly}(\text{AlaGly})_3\text{GluGly}]_{10}$  (**3**), which show that the dynamic behavior

of the glutamic acid residue  $C_{\alpha}$  remains unchanged upon crystallization, while the alanyl-glycine units exhibit behavior consistent with localization in crystalline  $\beta$ -sheets (Wang et al., 1996).

In summary, repetitive peptide sequences based on naturally occurring protein structural motifs have demonstrated the ability to form well-defined protein crystals with controlled surface chemical functionality. Preliminary investigations indicate that these structures form not only in the solid state, but also at the air/water interface. Further exploration of these materials will provide insight into both the nature of protein folding in solids and the formation of well-defined, unique protein architectures which can orient specific chemical functionalities or recognition sites at surfaces.

## 17.3 Helical Structures

Helical rods also form well-defined protein architectures, and have been explored for their ability, arising from their rod shape anisotropy, to form oriented materials and solutions. Poly( $\alpha$ ,L-glutamic acid) (PLGA) assumes a helical rod shape and has been used in studies of this shape anisotropy and its influence on material properties. The benzyl ester of this protein, poly( $\gamma$ -benzyl- $\alpha$ ,L-glutamate) (PBLG), has been used to form oriented films (Horton et al., 1990) and liquid-crystalline solutions (McMaster et al., 1991). As a result of the large dipole moment along the helical axis (Hol et al., 1978), electric fields can be used to orient such rod-shaped molecules. The resulting oriented materials exhibit interesting piezoelectric and nonlinear optical properties (Block, 1983).

The conventional method for preparing PLGA and its ester derivatives is via the ring-opening polymerization of *N*-carboxy-

$\alpha$ -amino acid anhydrides (Block, 1983). As with any traditional method of polymer synthesis, the resulting polymer has a broad molecular weight distribution, and the resulting heterogeneity in the helical lengths limits the liquid-crystalline structures and ordered architectures that can be formed. For example, PBLG is known to form cholesteric liquid crystalline phases, in which there is orientational order but no longitudinal registry of chains. On the other hand, smectic liquid crystalline phases, in which there is both orientational order and longitudinal registry, have not been observed for PLGA or its ester derivatives. In contrast, the tobacco mosaic virus, a naturally derived helical structure, will form smectic liquid crystalline phases in solution (Wen et al., 1989).

A monodisperse derivative of PLGA, the polypeptide H<sub>2</sub>N-GluAsp(Glu<sub>17</sub>Asp)<sub>4</sub>Glu-Glu-OH (**4**), was prepared biosynthetically using the bacterial expression vector pGEX-3X (Zhang et al., 1992). Aspartic acid was incorporated periodically to provide recognition sites for the restriction enzyme *Bbs*I without compromising the genetic stability of the repetitive glutamic acid sequence. Aspartic acid was chosen because of its structural and chemical similarity to glutamic acid, which should minimize structural perturbations (Zhang et al., 1992).

The purified polypeptide migrates as a single band in polyacrylamide gel electrophoresis, in striking contrast to the behavior of commercially available PLGA (polydispersity index 1.2), which shows a complete absence of discrete bands. The benzyl ester of **4** [a monodisperse derivative of PBLG (**5**)] was prepared by alkylation of the acid form of the polymer with phenyldiazomethane (Yu et al., 1997). The 500 MHz <sup>1</sup>H NMR spectrum of **5** is virtually identical to that of conventional PBLG, with the exception of two weak aspartic acid resonances. Integration of the spectrum indi-

cates 98% benzylation of the side chains of **4** (Yu et al., 1997). Optical micrographs of a 35% solution of **5** in a 97/3 mixture of chloroform and trifluoroacetic acid show an iridescent, fan-like texture suggestive of smectic order. Furthermore, small angle X-ray diffraction patterns of films dried from this solvent show a well-defined maximum spacing at  $114.5 \pm 1.4$  Å ( $11.45 \pm 0.14$  nm) and the corresponding second-order reflection at  $57.0 \pm 0.3$  Å ( $5.70 \pm 0.03$  nm) (Yu et al., 1997). The spacing of 114.5 Å (11.45 nm) is almost exactly the expected length of the monodisperse PBLG helix, a result that strongly suggests smectic-like ordering in the cast solid film. The phase behavior of these materials is being investigated further as a function of solvent, concentration, temperature, and chain length, and the ability of monodisperse macromolecular rods to form well-ordered surface layers is also being evaluated.

## 17.4 Hybrid Artificial Proteins

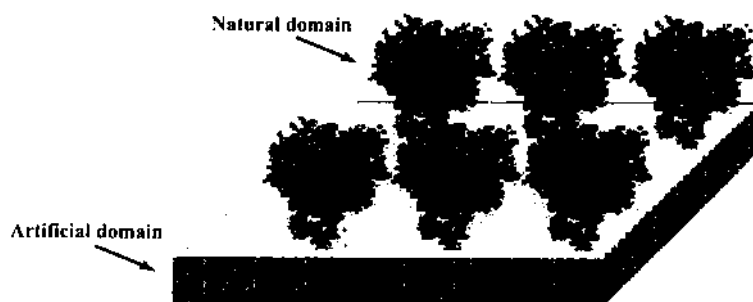
The formation of well-ordered architectures has the potential for controlling not only the spatial arrangement of polymers, but also the presentation of specific chemical functionality and molecular recognition sequences at interfaces. Precise and selective recognition of a guest by a host is a critical and necessary event in biological processes such as catalysis (substrate recognition by enzymes), immunological response (antigen-antibody interactions), virus infectivity, and cell adhesion. The high degree of selectivity and sensitivity exhibited by enzymes has been exploited in a variety of biosensor applications (Charych et al., 1994; Virta et al., 1995; Marx et al., 1994).

Several issues arise with the use of catalytic proteins as components of biosensors, however. The globular proteins, while ex-

cellent catalysts, have, in general, only marginal materials properties, which limit their use directly as materials and films. In addition, the thickness of an enzyme layer on a biosensor directly affects the coupling of the recognition event to the sensor element, and the homogeneity of the surface layer is of critical concern in optimizing sensor performance. Perhaps most importantly, control of the orientation of the active site of a molecule on a surface can have significant effects on the ability of the molecule to bind to its substrate (McLean et al., 1993; Chilkoti et al., 1995).

Biosynthetic methods for producing artificial proteins may provide a means to overcome these difficulties. The design of periodic sequences which exhibit controlled chain folding, crystal dimensions, and surface functionality on the length scale of 100 Å (10.0 nm), as described above, may be extended to optimizing the spatial positioning, orientation, and activity of a catalytically active site on a surface. This can be achieved through the synthesis of hybrid artificial proteins, as shown in Fig. 17-10, in which a natural domain with a catalytic function is linked to an artificial domain with the required materials properties. Possible applications include the immobilization of enzymes on surfaces in controlled orientations and density, as well as the preparation of catalytically active membranes, particles, and films.

There are several design factors to consider in preparing such materials. The artificial domain must contain functional groups for attachment to the surface of interest, and may also have the capacity to form ordered architectures. The functional group requirement can be satisfied by the incorporation of, for example, lysine, cysteine, glutamic acid, or aspartic acid residues into the protein chain. The protein sequence can be chosen to form either helical or  $\beta$ -sheet



**Figure 17-10.** Schematic representation of hybrid artificial proteins. The natural domain imparts biological activity, while the artificial domain imparts materials properties which can be used to form biologically active surface arrays, membranes, films, and particles.

structures to satisfy the second criterion. The periodic polypeptides described above satisfy both of these requirements and were therefore used as the artificial domain in our first generation of hybrid artificial proteins. It is envisioned that varying the length and number of repeat units in the artificial protein domain may permit control of the thickness of immobilized layers and the density of catalytic sites on a surface.

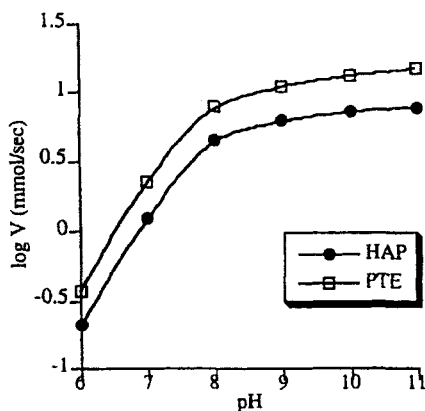
The natural (e.g., catalytic) domain of the hybrid must satisfy a completely different set of criteria. In general, the enzyme should retain function as a single polypeptide chain, which is not a trivial requirement given that many enzymes must form associated quaternary structures (comprised of two or more subunits) to exhibit activity. The enzyme selected should express well in a bacterial host, and tolerate modification by fusion to the artificial protein without loss of function. In our first experiments, *Pseudomonas diminuta* phosphotriesterase was chosen as the natural domain. This enzyme was previously cloned and expressed in an *E. coli* host, was in plasmid encoded form, and was known to tolerate modification at the *N*-terminus of the protein without loss of function (Dumas et al., 1989, 1990). Furthermore, this enzyme detects and detoxifies organophosphorus compounds, such as the pesticides parathion and diazinon, a function that could be useful in agricultural and consumer applications.

**Table 17-1.** Enzymatic activity of native and hybrid artificial phosphotriesterase.

	Phosphotriesterase	Hybrid Phosphotriesterase
Specific activity (units/mg)	7434	1976
$K_m$ ( $\mu$ M)	155	106
$k_{cat}$ (1/s)	6540	2315

Bacterial expression of hybrid phosphotriesterases has been achieved with the artificial domains  $[(\text{AlaGly})_3\text{GluGly}]_{36}$  (Dong et al., 1994) or  $[(\text{AlaGly})_3\text{ProGluGly}]_{16}$  (Wu et al., 1996) to yield catalytically active hybrid proteins. Table 17-1 and Fig. 17-11 indicate the similarity of the hybrid proteins to the native enzyme. Both exhibit Michaelis–Menten kinetics and, as shown in Table 17-1, have similar kinetic constants. The specific activity of the hybrid protein is lower than that of the native phosphotriesterase, though this is due in part to its higher molecular weight (55 kDa vs. 39 kDa for the phosphotriesterase). It is interesting to note that the Michaelis constant ( $K_m$ ) of the hybrid protein is lower than that of the phosphotriesterase, indicating a higher affinity of the substrate for the hybrid protein. Additionally, as shown in Fig. 17-11, the two proteins have matching activity–pH profiles (Wu et al., 1996), which indicates that the artificial domain does not significantly af-





**Figure 17-11.** pH-rate profile of paraoxon hydrolysis by native and hybrid phosphotriesterase. [Reproduced with permission from Wu et al. (1996).]

fect the key ionizable groups of the native enzyme.

Although the two proteins exhibit similar catalytic behavior, they exhibit very different affinities toward the anionic exchange resin DEAE-Sephadex A-50 (Dong et al., 1994). Cell extracts containing the proteins were loaded onto a column preequilibrated with 0.05 mM HEPES buffer (pH 8.5). The hybrid protein eluted at 0.3 M NaCl, while the native enzyme eluted even in the absence of salt. Addition of the pesticide paraoxon to the resin treated with the hybrid protein resulted immediately in the yellow color characteristics of the *p*-nitrophenol hydrolysis product. Resin treated with the native enzyme, however, exhibited no enzymatic activity due to the lack of enzyme retention after washing. These results indicate the bifunctional nature of the hybrid artificial protein, with the natural domain imparting catalytic function and the structural domain providing affinity for cationic surfaces. Current investigations are directed toward the immobilization of this enzyme on a variety of surfaces, including functionalized glass columns for use in flow injection analysis. This methodology can also be extend-

ed to include the immobilization of different recognition elements, such as antibodies and cell surface receptors.

## 17.5 Artificial Amino Acids

Molecular biological methods provide a powerful means to control the molecular size, composition, sequence, and stereochemistry of protein polymers. The demonstrated ability of these protein polymers to form unique macromolecular architectures and surfaces will be of certain importance in expanding the role of proteins as materials with interesting liquid-crystalline, crystalline, surface, electronic, and optical properties. Standard methods of *in vivo* protein synthesis, however, use only the 20 naturally occurring amino acids normally encoded by mRNA templates. As a result, there has been a great deal of interest in incorporating additional chemical functionality, including halogens, alkenes, alkynes, and electroactive substituents, into protein polymers.

There are three methods by which the incorporation of nonnatural amino acids can be achieved. One strategy involves simply the direct chemical synthesis of polypeptides containing artificial amino acids. Although this approach completely avoids limitations associated with the charging of tRNAs, the polymerization methods suffer from lack of control of the polymer structure, while solid phase chemistries are limited in terms of the molecular weight achievable.

A second approach, which offers more control over the polymer structure, entails a combination of chemical and biological synthesis (Noren et al., 1989; Bain et al., 1989; Mendel et al., 1991, 1992). In this method, the artificial amino acid of interest is chemically attached to a suppressor tRNA and then incorporated into the target protein

by *in vitro* translation. This method permits the introduction of artificial amino acids into specific sites, and the fact that the synthesis takes place *in vitro* (rather than in the cell) obviates the usual restrictions on the enzymatic charging of tRNA. This strategy is not suited, however, to producing large amounts of analog-containing protein, since the chemical acylation is often difficult and the tRNA is not recycled. Furthermore, the efficiency of suppression is generally about 50%, which limits the usefulness of the method for incorporating artificial amino acids at multiple sites.

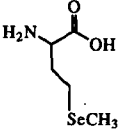
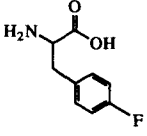
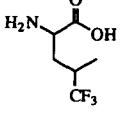
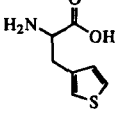
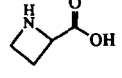
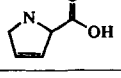
The *in vivo* incorporation of artificial amino acids, a third approach and the one used in our laboratory, permits the incorporation of analogs into multiple sites along a precisely designed protein polymer chain. The ability of the cell to incorporate artificial amino acids into proteins is evidenced by the incorporation of the amino acid analog selenomethionine (SeMet), which can be used in all steps of protein biosynthesis and can support cell growth (Tuve and Williams, 1957; Cowie and Cohen, 1957). Additional reports of the incorporation of more than 20 artificial amino acids, including *p*-fluorophenylalanine (pFF) (Cowie et al., 1959), norleucine (Fenster and Anker, 1969), and trifluoroleucine (tfL) (Richmond, 1963), indicate the ability of the bacterial host translational machinery to incorporate amino acid analogs which differ in structure and functionality from the native amino acids.

The key determinant of the success of the *in vivo* approach is the susceptibility of the analog to charging by the corresponding aminoacyl-tRNA synthetase. These enzymes are highly specific for each of the 20 natural amino acids and can distinguish between even chemically similar amino acids with little error (*vide supra*). The specificity of the enzyme requires that the amount

of natural amino acid present in the system be limited relative to the analog, so that analog incorporation is favored. A bacterial auxotroph (a strain that is unable to synthesize a particular amino acid) is therefore used for *in vivo* analog incorporation.

There are two procedures that can be used to incorporate an amino acid analog *in vivo*. If the analog (e.g., selenomethionine) will support cell growth, an *E. coli* auxotroph is used and grown on a medium supplemented with the analog rather than the natural amino acid. Artificial protein production is induced by standard methods, and the target protein is isolated and purified. In most cases, however, the analogs of interest will not support cell growth, so the auxo-

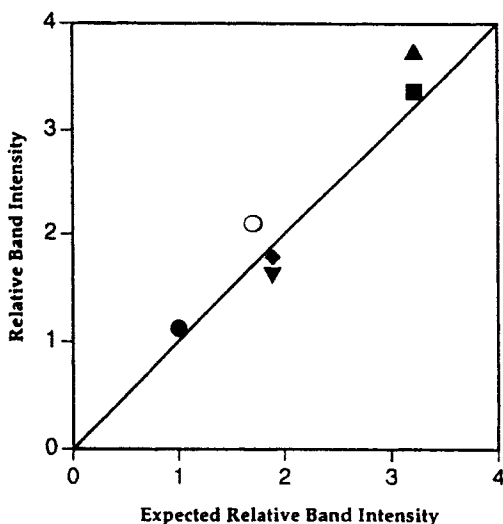
**Table 17-2.** Amino acid analogs incorporated into artificial protein polymers.

Name	Code	Structure
Selenomethionine	SeMet	
<i>p</i> -Fluorophenylalanine	pFF	
5,5,5-Trifluoroleucine	tfL	
3-Thienylalanine	3-TA	
Azetidinecarboxylic acid	Aze	
Dehydroproline	Dhp	

troph is grown first in a medium containing the natural amino acid (to increase the number of protein-producing cells). The cells are then centrifuged, washed quickly, and resuspended in a medium containing the analog but not the natural amino acid. Protein expression is then induced, and the protein isolated and purified. These methods have proven successful for incorporating a variety of artificial amino acid analogs (Table 17-2) into repetitive polypeptide sequences analogous to **1** and **2**, as described below.

### 17.5.1 Selenomethionine

Selenomethionine, due to its demonstrated ability to support *E. coli* cell growth, has been incorporated (in place of methionine) into the repetitive polypeptide [(GlyAla)<sub>3</sub>GlyMet]<sub>9</sub> (**6**) (Dougherty et al.,



**Figure 17-12.** Comparison of experimental and expected selenomethionine incorporation for the induced polypeptide at different ratios of selenomethionine to radiolabeled methionine. Experimental ratios were obtained by scanning autoradiographic signals. Expected ratios correspond to the intensities predicted if the incorporation of selenomethionine is equivalent to that of methionine at each concentration tested. [Reproduced with permission from Dougherty et al. (1993).]

1993) to demonstrate the incorporation of amino acid analogs into repetitive  $\beta$ -sheet proteins. A methionine auxotroph was prepared and transformed with the expression vector pGEX-9GM (Dougherty et al., 1993), which contained the DNA sequence encoding **6**. Determination of the level of selenomethionine substitution in the target protein was conducted via a competitive assay using selenomethionine and radiolabeled methionine. A decrease in radiolabeled methionine in the target protein was shown to correlate linearly with an increase in unlabeled selenomethionine in the growth medium. As shown in Fig. 17-12, the experimentally determined ratio of selenomethionine to methionine in the product correlates extremely well with the ratio of the amino acids in the medium, indicating near perfect replacement of methionine by selenomethionine (Dougherty et al., 1993). Furthermore, the transformed cells were shown to produce target protein when grown on a medium containing only selenomethionine, suggesting that 100% analog incorporation is possible.

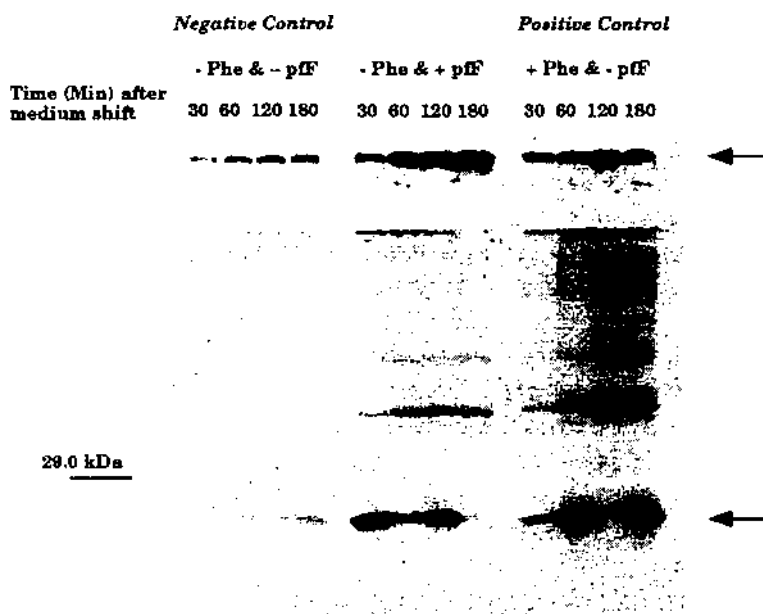
### 17.5.2 Fluorine

Fluoropolymers exhibit many unique and useful materials properties: low surface energy (e.g., teflon-coated pans), chemical and biological inertness (e.g., vascular grafts), low friction coefficient, excellent solvent resistance, and good hydrolytic stability. They therefore find uses as membranes, surface treatments, and biomedical materials. In an effort to capture some of these qualities in well-defined protein architectures, as well as to investigate the range of analog functionality that can be incorporated into artificial proteins, we have incorporated *p*-fluorophenylalanine (pfF) and 5,5,5-trifluoroleucine (tfL) into periodic polypeptides with sequences of the form

$[(\text{GlyAla})_3\text{GlyXxx}]_m$  (7) (Yoshikawa et al., 1994), where Xxx was encoded as Phe for pfF ( $m=13$ ) and as Leu for tfL ( $m=12$ ). These substitutions were expected to succeed because fluorine is similar in size to hydrogen and because many fluorinated amino acid analogs have been incorporated into proteins by *in vivo* protein synthesis (vide supra).

An expression vector [pET-13GF] (Yoshikawa et al., 1994) encoding the above sequence (with Xxx=Phe) was used to transform the appropriate *E. coli* auxotroph. The cells were initially grown in a medium containing the natural amino acid; they were then shifted to a medium containing the analog. Induced protein expression was monitored by the *in vivo* incorporation of  $^3\text{H}$  glycine and analyzed with SDS-PAGE, as

shown in Fig. 17-13. The results indicate the accumulation of target protein in the medium containing only the pfF analog (i.e., without Phe), indicating successful analog incorporation. A high level of incorporation was found for both analogs (Yoshikawa et al., 1994) as determined by  $^1\text{H}$  NMR spectroscopy and amino acid analysis (>95% for pfF and 88% for tfL). Furthermore, FTIR and WAXD studies of the protein solids confirm the antiparallel  $\beta$ -sheet architecture, suggesting that the fluorinated analogs reside at the lamellar crystal surface and may modify the surface properties of the crystal. Indeed, for the tfL analogs, advancing hexadecane contact angles increased from a value of  $17^\circ$  for the leucine derivative to a value of  $70^\circ$  for the derivative containing 88% tfL.



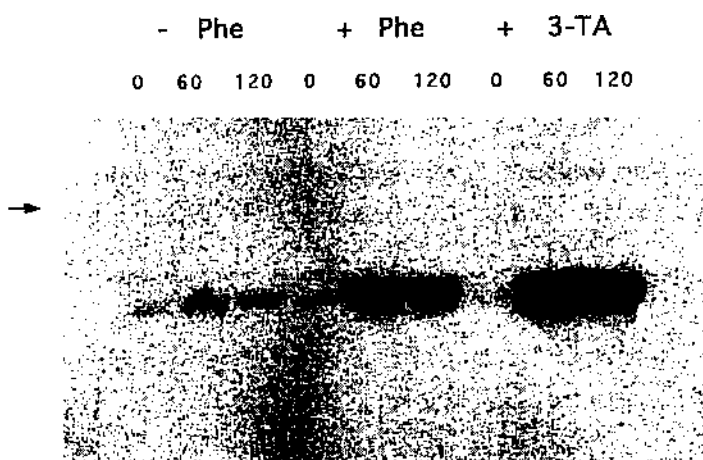
**Figure 17-13.** *In vivo* protein synthesis of  $[(\text{GlyAla})_3\text{GlyXxx}]_{13}$  with Xxx = Phe or pfF. Protein yields were compared after cultures were shifted to three different media 10 min after induction in the presence of the 20 natural amino acids. Lanes 1–4 contain protein from cells shifted to a medium lacking both Phe and pfF; in lanes 5–8, the medium lacks Phe but contains pfF; in lanes 9–12, the medium contains Phe, but not pfF. Time points are relative to the medium shift. Arrows indicate the target protein [Reproduced with permission from Yoshikawa et al. (1994).]

### 17.5.3 Electroactive Substituents

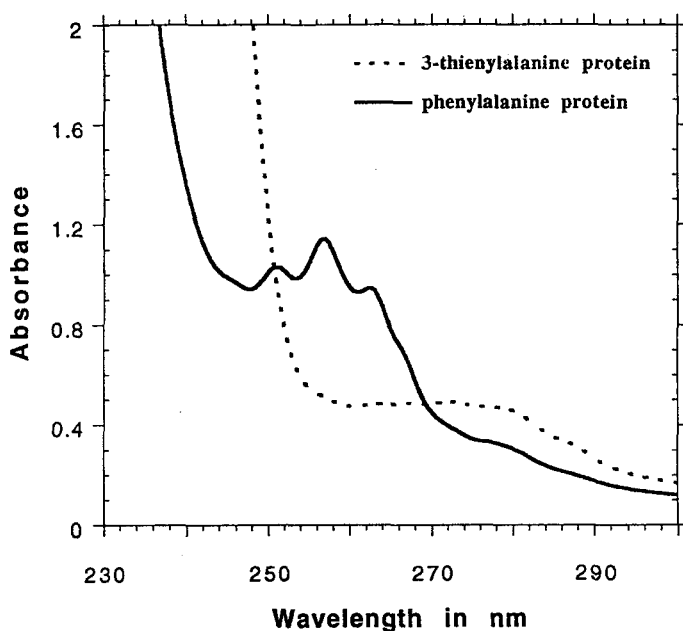
Conducting polymers have been actively investigated owing to their potential applications in lightweight batteries, electrodes, and nanowires. The production of conducting polymers, however, is often plagued by the insolubility of the highly conjugated, rigid polymer product. The incorporation of electroactive substituents into repetitive artificial peptides may help circumvent these difficulties. The artificial protein backbone could control the spatial organization of electroactive monomers to improve the degree of polymerization of the electroactive substituents and to control the spatial organization of the resulting conducting layers or domains. Additionally, this methodology may find use in the direct electropolymerization and attachment of enzymes to electrode surfaces.

To this end, we have prepared lamellar proteins containing 3-thienylalanine (Kothakota et al., 1995) (3-TA, Table 17-2) via the biosynthesis of polymers of structure 7, where Xxx is Phe,  $m = 13$ , and 3-TA is sub-

stituted for Phe in the growth medium. The choice of 3-TA for these studies was based on its chemical similarity to the 3-alkylthiophenes, which can be oxidatively polymerized through the 2- and 5-positions to produce extended conjugated systems. In fact, electrochemically doped poly(3-alkylthiophene)s are among the best conducting organic polymers, with measured conductivities as high as 2000 S/cm (Roncali et al., 1988). The protein sequence was encoded into the expression vector pET-13GF, and analog-containing protein was produced by shifting the cells from the initial Phe-supplemented medium into 3-TA medium. The accumulation of protein containing the analog is indicated in the electrophoretic data shown in Fig. 17-14. The ultraviolet spectrum shown in Fig. 17-15 demonstrates loss of the phenylalanine absorption in the target protein and provides a means to assess quantitatively the extent of analog incorporation. The extent of substitution of the 3-TA for Phe is approximately 85%, as assessed by UV spectroscopy in combination with amino acid analysis and  $^1\text{H}$  NMR spec-



**Figure 17-14.** In vivo protein synthesis of  $[(\text{GlyAla})_3\text{GlyXxx}]_{13}$  with Xxx = Phe or 3-TA. Lanes 1–3 contain protein from cells shifted to a medium lacking both Phe and 3-TA; in lanes 4–6, the medium contains Phe but not 3-TA; in lanes 7–9, the medium lacks Phe and contains 3-TA. Time points are relative to the medium shift. [Reproduced with permission from Kothakota et al. (1995).]



**Figure 17-15.** UV spectra of the polypeptide  $[(\text{GlyAla})_3\text{GlyXxx}]_{13}$  containing either phenylalanine or 3-thienylalanine as Xxx. [Reproduced with permission from Kothakota et al. (1995).]

troscopy. Evaluation of the electroactive film-forming properties of these 3-TA containing proteins is underway.

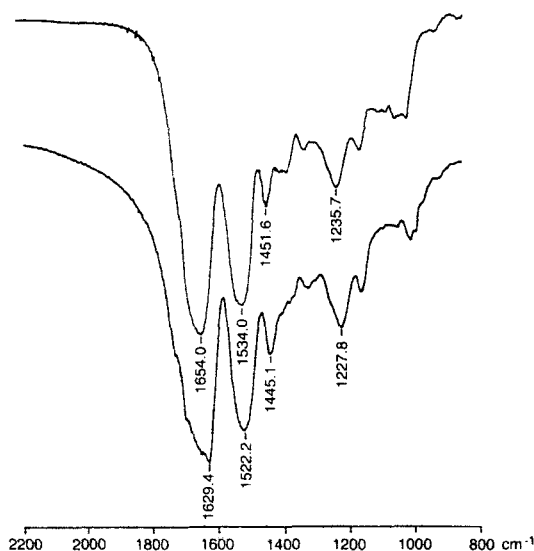
#### 17.5.4 Analogs for Structural Modification of Polypeptides

Polymers of repeating unit  $[(\text{AlaGly})_3\text{-ProGluGly}]$ , as described previously, have been successfully produced in *E. coli* hosts, but have proven to be difficult to crystallize (McGrath et al., 1992). The conformationally restricted proline residue, which is normally isolated at turn structures, may in the repetitive polymer prevent alignment and hydrogen bonding of the  $\beta$ -strands due to incorrect chain trajectories or steric bulk (vide supra). Therefore analog substitution at proline sites may promote folding of the repetitive proteins and provide surface sites for subsequent chemical modifications. That proline substitution can exert significant influence on protein folding has been demonstrated by the destabilization of the collagen

triple helix with the substitution of as little as 4% of azetidine-2-carboxylic acid (Aze) for proline (Lane et al., 1971).

Both Aze (Deming et al., 1996) and dehydropoline (Dhp) (Deming et al., 1997) variants of proteins of the sequence  $[(\text{AlaGly})_3\text{ProGluGly}]_{16}$  were expressed using an *E. coli* proline auxotroph. Incorporation of these analogs was predicted on the basis of previous studies indicating in vivo incorporation of many proline analogs into cellular proteins (Mauger and Witkop, 1966). The Dhp analog was the most readily incorporated (nearly 100%), while the Aze analog was incorporated at levels of approximately 40%, as determined by  $^1\text{H}$  NMR spectroscopy and amino acid analysis.

The physical properties of the Dhp variant are qualitatively similar to those observed for the proline form. Both form optically clear, amorphous solids and are water soluble, indicating a lack of crystallization. The chemical properties of the Dhp



**Figure 17-16.** Infrared spectra (FTIR) of the polypeptide  $[(\text{AlaGly})_3\text{ProGluGly}]_{16}$ , as KBr pellets, containing only proline (top) and azetidinecarboxylic acid (bottom). [Reproduced with permission from Deming et al. (1996).]

variant, however, are significantly different. Reaction of the Dhp variant with  $\text{H}_2\text{O}_2$  or  $\text{Br}_2$  produces hydroxylated and brominated forms of Dhp in a quantitative reaction, as assessed by amino acid analysis and by loss of the alkene resonance in the  $^1\text{H}$ NMR spectrum (Deming et al., 1997). The incorporation of alkene functionality in artificial proteins provides a strategy for incorporating these and other novel functional groups into the appropriately engineered protein chains.

Analysis of the solid state structure of the Aze variant of the protein by FTIR spectroscopy yields the results shown in Fig. 17-16. The amide I and II absorptions at 1629 and 1522  $\text{cm}^{-1}$ , respectively, in the Aze protein (bottom spectrum) confirm a  $\beta$ -sheet structure (Deming et al., 1996). The proline form of the polypeptide, in contrast, exhibits amide I and II bands at 1654 and 1534  $\text{cm}^{-1}$ , indicative of conformational disorder. The smaller Aze analog appears to increase

chain flexibility enough to permit efficient folding. That substitution of only 4–6 amino acids out of a total 148 can cause such a striking change in the folding of the polypeptide chain has important use in the study and control of sequence–structure relationships in protein polymers.

## 17.6 Conclusions

The biological synthesis of protein polymers is a powerful strategy, with no conventional polymer synthesis counterpart, for producing macromolecular materials in which the molecular weight, composition, sequence, and stereochemistry are all controlled essentially absolutely. This methodology has been used to produce unique protein polymers which form well-ordered crystalline and liquid-crystalline structures. These macromolecular structures can be regulated on length scales of tens of nanometers and exhibit controlled surface chemistries. Biologically active molecules have been fused to such artificial proteins with the retention of biological activity, demonstrating the potential for forming new hybrid materials by varying the properties of either domain. Finally, the repertoire of chemical functionality which can be included has been expanded by incorporating artificial amino acids into polypeptides using the existing protein biosynthesis machinery. Halogen, alkene, and electroactive functional groups have been incorporated into protein polymers to impart unusual surface properties and electrochemical behavior. These results point to the enormous potential of biosynthetic methods in designing novel polymeric materials which form self-assembled structures on nanometer length scales, exhibit desirable and optimized molecular recognition capabilities, and show valuable chemical and electrochemical behavior.

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## 18 Application of a Modular Approach in Polymer Science: Synthesis of a Broad Variety of Amphiphilic Block Copolymers

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## List of Symbols and Abbreviations

$A_m$	stabilized interface area per molecule
$d$	hydrodynamic diameter
$D_h$	diameter
$M_w$	weight-average molecular weight
$M_n$	number-average molecular weight
$M_{PB}, M_{PS}$	molecular weight of polybutadiene, polystyrene
$N_c$	length of core-forming block
$N_s$	length of outer dissolved block
$N_{PB}, N_{PS}$	length of polybutadiene, polystyrene block
$P$	pressure
$s$	scattering vector of small angle X-ray scattering
$S$	relative amount of surfactant
$T$	temperature
$T_c$	transition temperature
$T_g$	glass transition temperature
$V_e$	volume
$V_m$	monomer volume
$Z$	aggregation number

$\gamma$	surface tension
$\delta$	Hildebrandt parameter
$\lambda$	wavelength
$\sigma$	relative width

ABC	amphiphilic block copolymer
Alc	alcohol
9-BBN	borabicyclo[3.3.1]nonane
BC	benzoyl chloride
Chol	Cholesterol
DLS	dynamic light scattering
DMF	dimethylformamide
DNS	desoxyribonucleic acid
DSC	differential scanning calorimetry
GPC	gas permeation chromatography
IR	infrared
MBT	mercaptobenzothiazole
MCPBA	meta-chloroperbenzoic acid
MP	mercaptopyridine
NMR	nuclear magnetic resonance
Nu	nucleophile
P4VP	poly-4-vinylpyridine
PDLC	polymer dispersed liquid crystal
PDMS	polydimethylsiloxane

Pht	phthalic anhydride
PSB	polystyrene- <i>b</i> -polybutadiene
PTFE	polytetrafluoroethylene
Pyr	pyrazine-2,3-diacid anhydride
SAXS	small-angle X-ray scattering
THF	tetrahydrofuran
UV	ultraviolet
WAXS	wide-angle X-ray scattering

## 18.1 Introduction

Modern polymer chemistry involves the design of monomer units and polymer architecture, the control of molecular weight and its distribution, the layout of polymer composition by comonomers, and the control of their statistical distribution. It is generally true that handling these different molecular parameters is difficult. Consequently, a controlled layout of a more complex polymer molecule involving complicated functional groups remains even nowadays in many cases still a dream.

To bypass the problem of designing new monomers for each application as well as to decouple the problems of controlling chain length, statistics, and architecture from the chemical layout (functionality, polarity) of the polymer, a so-called modular approach towards targeted polymer entities may be considered.

We define here the underlying principles of this modular approach and demonstrate its applicability with the synthesis of a number of different, highly valuable amphiphilic block copolymers of the (ABC) type. These polymers can be regarded as a special class of advanced surfactant and are tailor-made to stabilize a number of technologically relevant interfaces, i.e., in the present case the air/polymer interface, the metal/polymer interface, and the interface between polymer and ceramic material.

To demonstrate the principles of a modular synthesis, all ABCs are made from the same simple precursor polymer, which defines the structure and architecture. This polymer is coupled via polymer-analogous reactions with diverse binding “units”, which are small functional organic molecules selected for their “philicity” to a certain interface. Once these molecules are attached to the polymer, they are responsible for fulfilling the material’s function.

The ABCs spontaneously aggregate to micelles, and this can be regarded as the most simple modular system, a polymer superstructure containing compartments with special properties (such as binding). As a result of these properties, a third component can be immobilized and stabilized in the micelle core, i.e., metal colloids or microdroplets of a liquid-crystalline phase. This binding as well as some of the resultant material properties of the final ternary system are also discussed.

## 18.2 Concepts

Modules have long been used in engineering to tackle problems of large complexity, either in the construction of mechanic or electronic devices or in the layout of modern software. We recall the development of modern computers, where the invention of a motherboard and cards with a variety of functions has become a part of our daily life. This was not the way that early computers were constructed!

During its design, a modern engineering device is split into functional subdevices called modules which themselves may consist of further subdevices. This way, an engineering hierarchy of functional structures is created. A module is defined by its function and its interface. Advantages of the modular approach are

- decreasing complexity as the module is divided into different levels,
- tests, corrections, and changes can more easily be performed,
- clarity of function, and
- moduli, one created, can be used in and exchanged between the different devices.

Software engineering is also a classic example where the use of modules has become necessary for designing modern complex

operating systems or programs, with the result that so-called modular programming is now a matter of course in computer sciences.

Like engineers, chemists face similar problems when they have to synthesize molecules or materials that simultaneously fulfill a variety of functions. This can be done by assembling a number of functional components into a device. The synthesis of such functional components and their assembly has become the domain of 'supramolecular chemistry', where chemists are able to design impressive supermolecules. Concomitant with the synthesis of ever larger molecular structures, the drawbacks of this approach become apparent. In many cases

- the synthesis of such molecules occupies increasingly large groups of synthetic chemists,
- for each single problem a single tailor-made molecule has to be synthesized, and
- the costs for such materials are enormous.

This is in some ways reminiscent of the days of writing 'spaghetti' programs to create complex software. The advantages of a modular approach in both cases are obvious.

In a similar manner as the wide-reaching development of new concepts and words in soft- and hardware engineering, the terms "modular chemistry" and "chemical system" have become popular in recent years, but due to their usage in very different contexts both certainly need definition.

Modular chemistry is closely related to the concepts of supramolecular chemistry introduced by Lehn (1995) or the concept of "integrated chemical systems" as described by Bard (1995). Characteristic for the approach described here is the prefabrication of subunits, which are coupled via simple chemical reactions and align either spontaneously or under special conditions to larg-

er superstructures. The consensus in the literature about this approach is recognized by comparing two definitions from the literature. Bard defines an integrated chemical system as "a heterogenous multi component system involving several different components designed and arranged for specific functions or to carry out specific reactions and processes. Usually it is the interaction of the components of the integrated chemical system that determines its properties" (Bard, 1995). The corresponding "molecular devices" of Lehn are defined as "functionally integrated chemical systems; they are based on specific components arranged in a suitable manner. The function performed by a device results from integration of the elementary operations executed by the components" (Lehn, 1995).

A definition restricted to the field of organic chemistry is found in Kaszynsky et al. (1992), where only molecular subunits (i.e., shape persistent molecules) are approved to create the object or superstructure, and the shaped objects do not necessarily have a function (other than appearance); the philosophy behind it is nevertheless regarded to be similar.

### 18.2.1 The Chemical Module

To avoid misunderstandings, the terms component, module, modular system, and modular chemistry are fixed in a hopefully tight enough definition to allow a precise but not restrictive use of them in practice.

Components or units that participate in a chemical reaction or structure formation are not necessarily low molecular weight molecules, such as in supramolecular chemistry, but can be larger objects, such as proteins, colloids, or polymers. If this component consists of more than one structural element or includes more than one chemical or physical functionality, we call it a chemical mod-

ule (even when it is still a “simple” organic molecule). A module should be understood as a subunit, which is easily coupled to the rest of the structure or replaced without major expenditure, either in the final structure or throughout the course of synthesis.

Lehn defined his elementary units to build up larger structures in a similar fashion, but called them components (Lehn, 1995). He further distinguished between functional, structural, and ancillary components, all of which are required for the related chemical system to produce the variety of targeted functions.

### 18.2.2 The Chemical System

A number of such moduli constitutes the chemical system. It is only possible to create the chemical system from a module (unimodular system) with phenomena or approaches like micelle formation (physical linking) and repetitive synthesis (covalent linking) leading towards complex organic molecules (Liess et al., 1996). On the other hand, the chemical system can contain diverse moduli with diverse functions (hetero- or multimodular system, the more general case).

To differentiate a chemical system from simple phase formation or random clusters, it should be a self-contained object with size, shape, composition, and function (or a combination of these quantities). The binding or linking of moduli does not usually require covalent bonds and in supramolecular chemistry is performed via reversible bonds such as strong hydrogen bridges, complex formation, or amphiphilic aggregation to the system. All these binding types allow the construction of more or less stable chemical systems, as well as the formation of ordered equilibrium structures.

For the synthesis of more stable, complex organic molecules or the desired polymer

structures, simple covalent bonds can also be employed, which are formed and split in high yields and selectivities, e.g., esterifications or sulfur bridges. The synthetic chemist can also use nature as a guide in this respect.

This modular building principle towards complex structured matter is illustrated in Fig. 18-1.

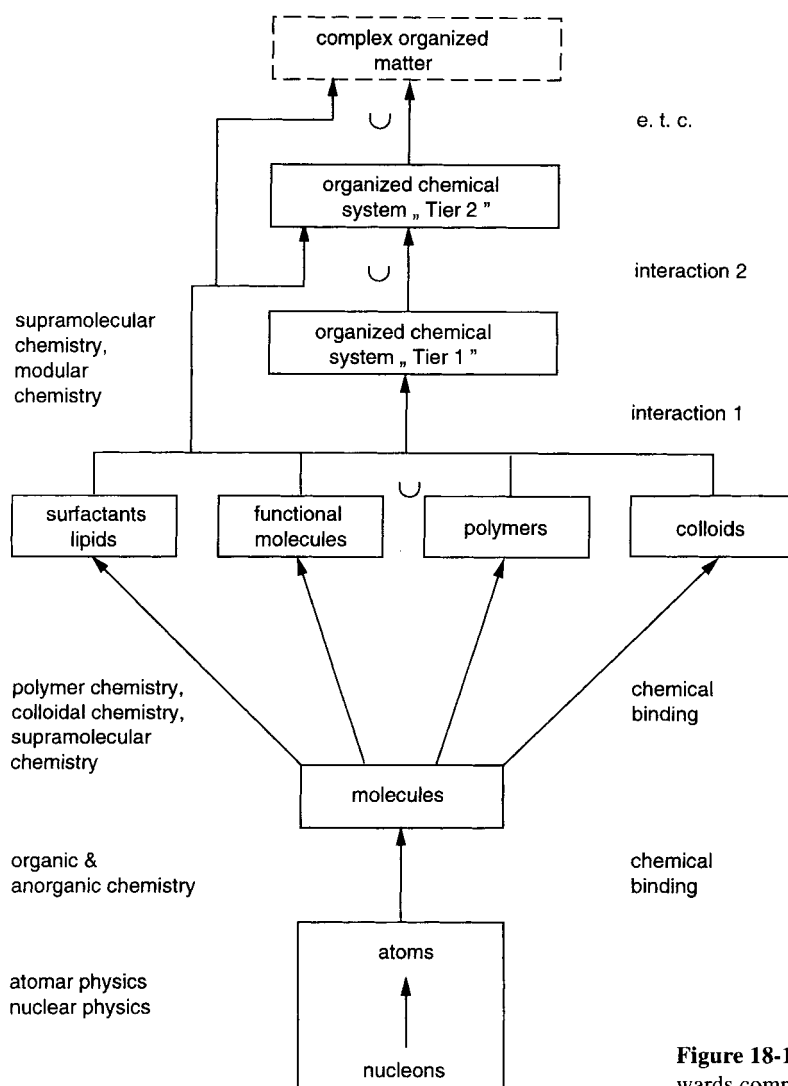
It is worth mentioning that in each step the type of binding for a modular system with more than one tier of hierarchy has to be switched to avoid negative structural interference between the different steps of integration. Having used in a first step, for instance, simple covalent bonding we have to consider another type of bonding in the second tier, i.e., stacking, amphotropic self aggregation, or a different type of simple covalent bond.

A very good example from nature is the construction of chromatin, which is used for the safe but dense storage of information, which within the language of modular chemistry is a “tier 3” structure. Four different histones (small spherical proteins) aggregate via hydrophobic interactions initially to dimers and then to octamers (tier 1). These octamers exhibit outer base functionalities, which bind segments of the acid DNS (tier 2). The resulting chain of pearls winds itself into a superhelix with five protein-DNS complexes per pitch (tier 3), which is due to secondary valences and the minimization of interface energy (see added reference below).

### 18.2.3 Targets of Modular Chemistry

Compared to the other methods of synthesis, modular chemistry is designated for a number of aims:

- 1) It enables simplified access to complex molecules via implementation of repeating, preconstructed moduli (repetitive synthesis



**Figure 18-1.** The structure hierarchy towards complex structured matter.

or prefabricated molecular construction). The exchange of a single module results in the synthesis of a new system without multiplication of the synthetic efforts. The complexity of the reaction schemes involved in each step of integration should be kept as low as possible.

2) It should be possible to generate new properties and property combinations by the utilization of a structure hierarchy above the level of simple molecules or polymers, i.e.,

the employment of the chemical system's properties.

3) Also planned is the construction of heteromodular composites to overcome classical borders between materials on a mesoscopic scale, e.g., hybrids between metal, ceramics, and polymers. The molecular connection between the moduli and the chemical handling of the related interface is expected to bring in a number of special properties, which exceed the corresponding ones



of the simple moduli, such as the ability to tailor synergistic properties.

4) Compartmental sharing of functions: As demonstrated by many biological systems, a heteromodular system can show a unique combination of functions by chemically arranging a “molecular team”. Here, any “specialist” module brings in special property into the team (e.g., stability, recognition, selective binding, hardness, special optical and magnetic properties, etc.). The chemical system is then equipped to fulfill a complex task, which is too complicated for an individual molecule to perform. Possible examples are selective binding and the conversion of a substrate, or the molecular recognition and conversion of optical and electrical signals.

5) A long-term objective is the controlled construction of synthetic matter over more than one step of integration for the generation of more effective and intelligent materials.

While modular chemistry is certainly a part or a further development of supramolecular chemistry (depending on the point of view), some of these aims also allow for differentiation. Exchangeability and the required search for maximum simplicity in each step of integration certainly belong to the key aspects of a modular approach. Characteristic for the modular approach is also the importance of the moduli's function and their interfaces.

Such standardized moduli if commercially available would greatly enhance the design of complex chemical devices, but seem to be only a vision of the distant future. The current task is to test whether such a modular approach may become feasible. At the top of the list for the design of a modular system are the mechanical and optic prop-

erties of elasticity and transparency, and functions like magnetic or electronic addressability. These functions have to be assigned to the different moduli, which must then be synthesized.

Next, all the components have to be organized on the modular level. Here it is helpful to have a structured and structuring environment which is able to incorporate these components much as a computer ‘motherboard’ provides the basis for electronic modules (cards) or a main program. The design of such a structured hierarchy at the modular level may appear a complicated task, but it is not really. Nowadays the knowledge of self-assembly, e.g., in lyotropic or thermotropic systems, enables chemists to design complicated structured environments on just the right length scale necessary to incorporate moduli, i.e., in the size range between 1 nm and 250 nm. The important point is that on each level of this hierarchy or in each module the complexity is kept as small as possible. This is necessary for the efficient production of such a device.

In the following, one possible approach to such structured environments will be delineated by means of the self-organization of amphiphilic block copolymers, which results in morphologies that allow the incorporation and addressing of other diverse components.

### **18.3 A “Plastic” Example: Amphiphilic Block Copolymers (ABCs), Their Micelles and Phases, and Material Hybrides Based on ABCs**

In the following, we will use the modular approach for the synthesis of polymers and polymer systems in two ways: First we will

employ a modular synthesis (still involving simple organic molecules with functionality) for the generation of very different types of amphiphilic block copolymers (ABCs) with high interface activities, which are effective for heterophase stabilization by modular exchange of one single reactant in polymer synthesis. Secondly, it will be demonstrated that these ABCs can act as modules by themselves and form a simple version of a modular system, since they exhibit lyotropic self-assembly towards micelles and more complex mesophases which offer interesting chemical perspectives.

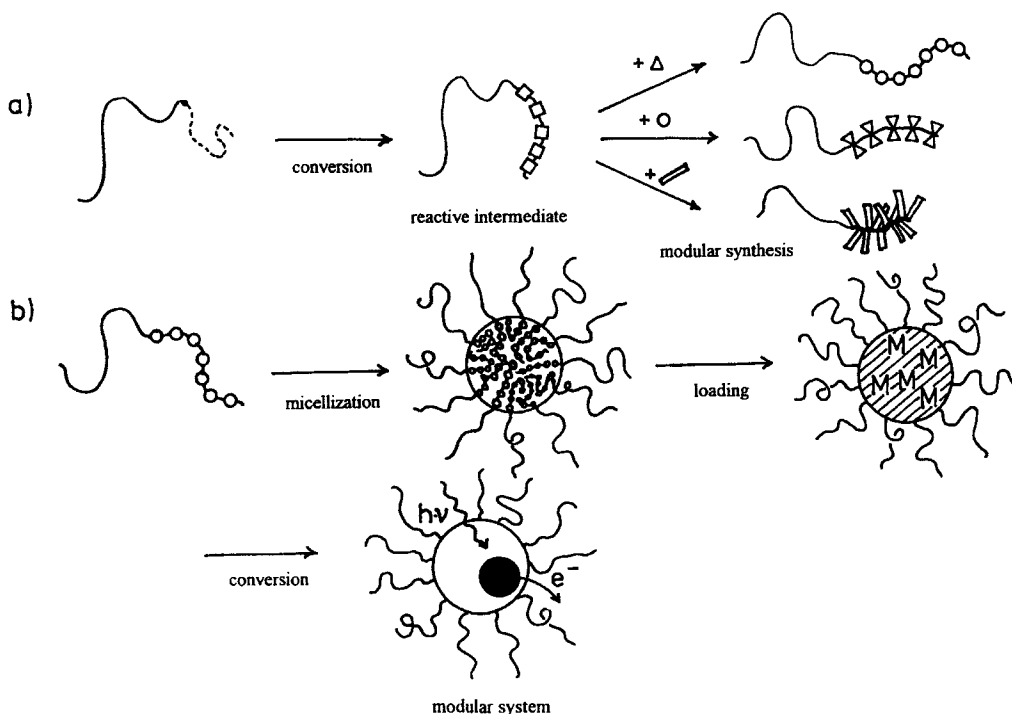
The current approaches to the production of ABCs usually require "living" polymerization techniques, such as anionic (Szwarc, 1983), cationic (Kennedy and Iván, 1991), or group transfer polymerization (Brittain, 1992). In the case of two polymerizable comonomers, the block copolymers may be synthesized directly. Usually, one component cannot be directly polymerized according to a living mechanism, and macromonomer synthesis (Tezuka, 1992; Meijs and Rizzardo, 1990), chain transfer or termination (Chung and Solomon, 1992; Riess et al., 1985) for the generation of special end groups, and reinitiation are applied. In most cases, high purity during the reactions, tedious isolation procedures, and/or the use of protecting group chemistry are required. This makes ABCs, apart from a few exceptions like polyethyleneoxide-*b*-polypropyleneoxide, very expensive and prohibits broader application.

Application of the described modular approach, which at this level is still a simple polymer-analogous reaction, enables a more simple synthesis of such polymers and definitely broadens the diversity of a variety of systems. The schematic working principle of such a modular synthesis towards differentially functionalized amphiphilic block copolymers (tier 1) and a modular

chemistry with block copolymers (as stabilizers and "connectors", tier 2) is shown in Fig. 18-2.

We start from a regular, cheap, and easily available block copolymer (in our case polystyrene-*b*-polybutadiene block copolymers) with defined chain lengths, composition, and structure, which is transferred via simple polymer-analogous reactions (epoxidation, hydroboration) into a reactive intermediate preserving the molecular characteristics. This reactive intermediate is reacted in a second step, which is almost free of side reactions (ring-opening of an epoxide, esterification), with a broad variety of differently functionalized, low molecular weight components to give the desired variety of amphiphilic block copolymers (tier 1).

The resulting block copolymers form micelles, the function of which is related to the binding modules of the inner core. Such micelles can be employed as "molecular reaction flasks" or "molecular transporters", i.e., it is possible to incorporate reactants inside the core and to react them with something with a very different polarity or chemical nature from the outside (generalized phase transfer catalysis). Another possibility lies in the implementation of reduction or precipitation reactions inside these molecular reaction flasks to produce solids with restricted dimensions, i.e., colloid particles with some special functions. Opening of the ABC aggregates in the presence of an interface with high interfacial energy and rearrangement of the ABCs in proximity of the interface results in lowering of the interface energy and a mechanically stable "glueing" of both phases on a molecular level. With regard to these applications, the phases and micelles of ABCs may serve as the "motherboard" of a modular system as well as the molecular "connectors" which regulate the "interface" to other moduli.



**Figure 18-2.** Schematic principle of a modular synthesis of amphiphilic block copolymers. ABCs as modules can form a modular system via aggregation and loading of the micelle core with functional secondary components.

At this stage, some explanatory remarks should also be given as to why it is important to find new synthetic pathways to amphiphilic block and graft copolymers. For instance, these polymers are discussed as candidates to substitute low molecular weight surfactant molecules in many heterophase stabilization problems, such as in emulsion polymerization or for the formulation of cosmetics and drugs. The advantages of polymers are obvious: As high molecular weight components, their critical micelle concentration can be kept extremely low so that they retain their efficiency even at high dilution. Furthermore, washing out and release to the environment are slowed down. For some technological applications, it is interesting to mention that the kinetic stability of the aggregation struc-

tures also responds to the chemistry and block length. Compared to the millisecond exchange of low molecular weight aggregates, the lifetime of block copolymer micelles can easily be adjusted to the second, minute, or hour region.

Particularly with amphiphilic block copolymers, it is possible to speculate about a "generalization of amphiphilicity", i.e., to design molecules that get attracted, and stabilize not only the oil–water interface (the classical problem of amphiphiles), but any interface between different materials with different cohesion energies or surface tensions. In this context, it is remembered that the compatibilization of polymer blends and the stabilization of filler particles or dye pigments can also be expressed as a problem of interface stabilization. The objective

of an adjustable amphiphilicity, however, requires careful choice of both the solvating as well as the binding block of the ABC molecule.

### 18.3.1 The (Modular) Synthesis of ABCs by Polymer-Analogous Reactions

As a result of their good accessibility in a variety of compositions and molecular weights with narrow molecular weight distribution, the low price, and their widespread use in technology, polystyrene-*b*-polybutadiene block copolymers were selected as the starting material. It is repeated that the choice of the polymer predetermines the polymer architecture, its absolute length, and the relative block lengths; the following chemical steps are designed to change the chemistry of both blocks but not the molecular architecture (decoupling of structure and functionality control).

For transfer into a reactive intermediate, the epoxidation reaction of the double bonds of the polybutadiene block was chosen. It is known from the literature that some simple epoxidation agents can be used where close-to-complete conversion with a tolerable amount of side reactions, such as crosslinking, is obtained (Antonietti et al., 1996a; Brosse et al., 1979; Iraqi and Cole-Hamilton, 1992). Another very versatile possibility of functionalization lies in hydroxylation via hydroboration with 9-BBN (9-borabicyclo[3,3,1]nonane), followed by oxidation with  $\text{H}_2\text{O}_2/\text{NaOH}$  (Ramakrishnan, 1991).

Following the epoxidation, a variety of opening reactions of the oxirane ring, such as the nucleophilic ( $\text{Nu} = \text{nucleophile}$ ) ring opening (Chini et al., 1990) and the reaction with acid chlorides (Nishikubo and Kameyama, 1993), are applied to introduce a widespread range of different functional side groups via simple low molecular weight reactants. For the hydroxy derivative, simple

esterification with a functional acid chloride or acid anhydride results in the targeted structure (Giménez et al., 1996; Frey et al., 1986).

Optimization of the epoxidation reaction of polystyrene-*b*-polybutadiene block copolymers is described in the literature (Antonietti et al., 1996a). Attempts to epoxidize the polybutadiene blocks with methyltriocetylammmonium-tetrakis(diperoxotungsten)-phosphate(3-) and  $\text{H}_2\text{O}_2$  failed (Jian and Hay, 1991). In this case, GPC measurements of the oxidized samples showed that an unacceptably high degree of crosslinking or insoluble polymers was obtained. Better results were obtained with the epoxidation by MCPBA (meta-chloroperbenzoic acid) in toluene. The molecular parameters of the epoxidized block copolymers were determined by DMF-GPC, IR spectroscopy, and  $^1\text{H}$ -NMR spectroscopy. The NMR spectra of the products no longer show any olefinic proton signals, which indicates an almost quantitative epoxidation. The GPC measurements, which are shown below, prove that only a small amount of high molecular weight (crosslinked) polymer is formed. Udipi (1979) proposed an acid-catalyzed, crosslinking reaction during the epoxidation process forming high molecular weight polymer. Solvent and concentration have a strong effect on the degree of crosslinking. Several other solvents were tested (e.g.,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ), but toluene turned out to be the best.

None of the epoxidized block copolymers showed micelle formation in THF or toluene. This was expected, since both blocks exhibit very similar cohesion energies in this case, i.e., they are of similar hydrophobicity.

In the case of hydroxylation of our polystyrene-*b*-polybutadiene block copolymers, we used a refined one-pot reaction from Ramakrishnan (1991).  $^1\text{H}$ -NMR measure-

ments showed that the hydroxylation is almost quantitative (no olefinic proton signals). In addition, no high molecular weight polymer was found by DMF-GPC measurements. Here we only changed the chemical nature of the polymer and not its architecture.

The resulting polystyrene-*b*-polyalcohol block copolymer is already very amphiphilic. Micelle formation was observed in toluene,  $\text{CHCl}_3$ , THF, and methanol.

In a second step, we modify the polyepoxide blocks by ring-opening reaction with several nucleophiles and acid chlorides, whereas the polyalcohol blocks are esterified with corresponding acid chlorides. For better illustration, some of the related structure formulas are sketched in Fig. 18-3.

It is shown that modification with appropriate nucleophiles quickly results in multifunctional organic substituents. The derivatives a) and b) are made for the stabilization of metal surfaces; c) and d) prefer alkaline earth salts and ceramic surfaces. The esterification with cholesterol e) not only results in a liquid-crystalline block copolymer, but also enables coupling to hydrophobic components. Interestingly, modification with acid chlorides is not restricted to hydrocarbon acid chlorides and perfluorinated derivatives can be effectively coupled, too (f). This gives rise to a block with ultra-hydrophobic character, a property that will be explained below.

The resulting products were characterized by  $^1\text{H}$ -NMR, IR and (whenever possible) DMF-GPC. The relative intensities of the NMR signals are in good agreement with the expected values. Completeness of modification is also confirmed by the absence of epoxy group proton signals and hydroxy group signals in NMR and IR spectroscopy. DMF-GPC measurements were only possible for polymers where DMF is a homogeneous solvent. Figure 18-4 shows some

typical GPC data throughout the course of the modification reactions. Here, the modular synthesis of polystyrene-*b*-poly(benzoic ester) as an analyzable model reaction is followed.

It is seen that the original molecular weight distribution stays practically unaffected. Only a minor peak with twice the molecular weight has been built up. The employed polymer reactions are obviously practically free of side reactions, and the required decoupling of structure and functionality control is given.

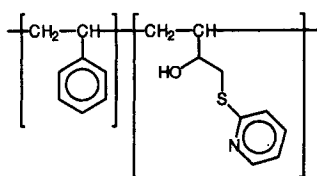
It is interesting to note that these polymer analogous reactions are not solely restricted to one block but can be performed on both blocks in a different but selective manner. This was performed during the synthesis of polyethylethylene-*b*-polystyrenesulfonate block copolymers, a very powerful electrosteric stabilizer for emulsions and suspensions (Tauer et al., 1997), the description of which is omitted here.

### 18.3.2 Micelles of ABCs

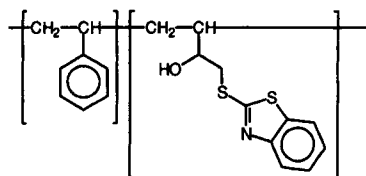
The amphiphilicity of all polymers is simply visualized by their ability to form micelles. This is quickly tested by dynamic light scattering (DLS), thus resulting in a hydrodynamic radius and distribution, as

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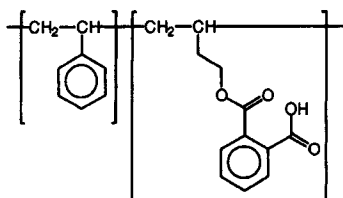
**Figure 18-3.** Structure formulas of some of the ABCs synthesized via the addition of commercial nucleophiles or esterification with acid chlorides: Modification of the polyepoxide block with a) 2-mercaptopyridine and b) 2-mercaptobenzotiazole. Esterification of the polyalcohol block with c) phthalic anhydride and d) pyrazine-2,3-diacid anhydride. Esterification can also be performed with liquid-crystalline derivatives such as e) cholesterol or f) ultra-hydrophobic moieties such as perfluorooctanoic acid. A very effective electrosteric stabilizer is g) the polyethylethylene-*b*-polystyrenesulfonate block copolymer. Block lengths for PSB-II:  $N_{\text{PS}} = 423$ ,  $N_{\text{PB}} = 390$ . The 1,4-content in the polybutadiene block is ca. 10%.



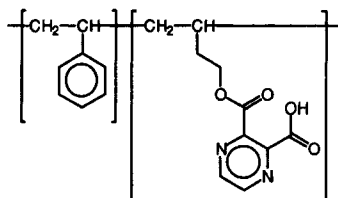
a) MP-PSB-II



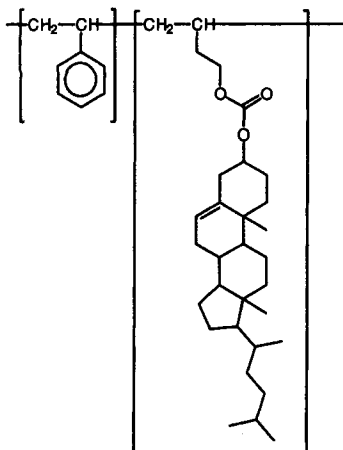
b) MBT-PSB-II



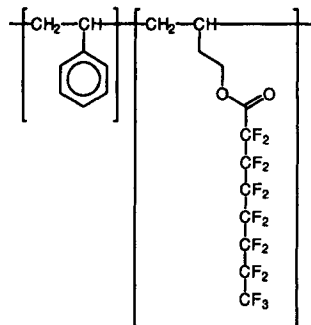
c) Pht-PSB-II



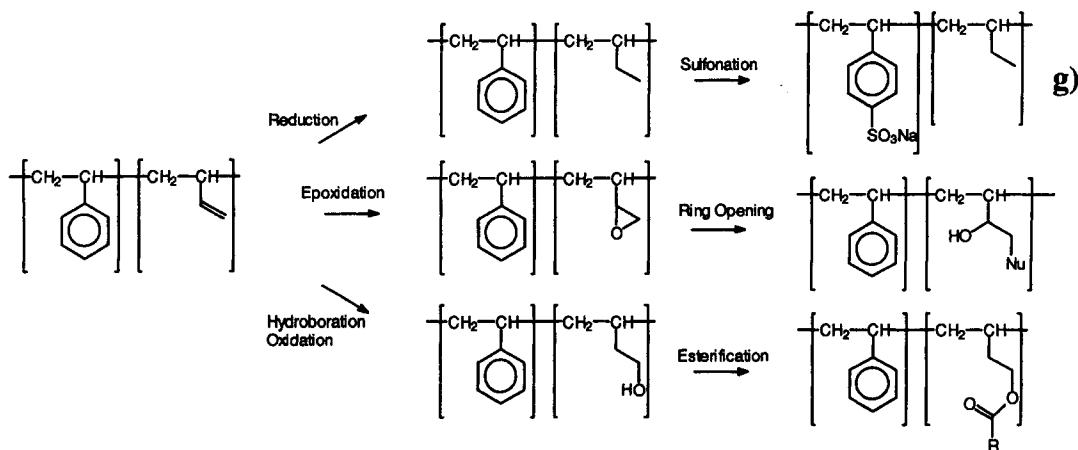
d) Pyr-PSB-II

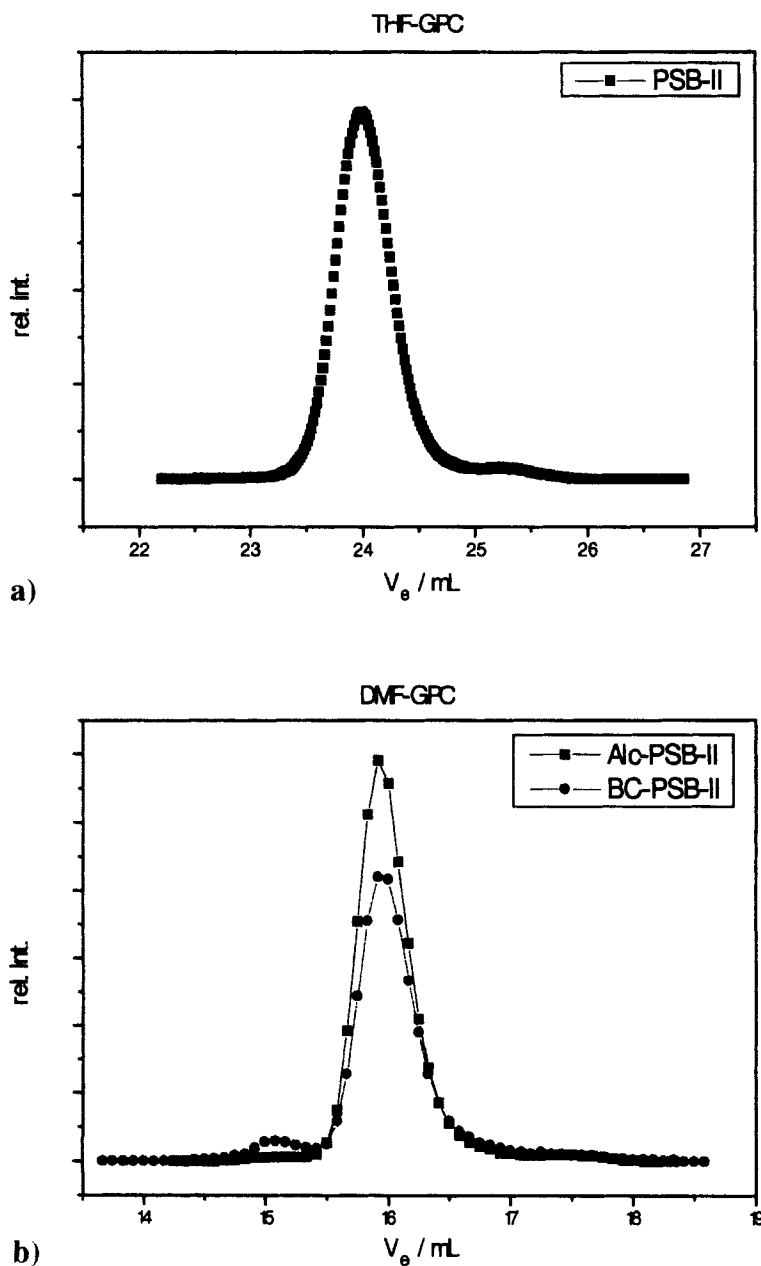


e) Chol-PSB-II



f) Fluoro-PSB-II





**Figure 18-4.** a) THF-GPC elugrams of polystyrene-*b*-polybutadiene block copolymer (PSB-II,  $M_w/M_n = 1.02$ ). b): DMF-GPC elugrams of polystyrene-*b*-polyalcohol block copolymers (Alc-PSB-II,  $M_w/M_n = 1.05$ ) and the resulting product after esterification with benzoyl chloride (BC-PSB-II,  $M_w/M_n = 1.07$ ).

well as with electron microscopy, which can depict the micelles' quality.

Micelle formation is obtained in selective solvents, i.e., of the polymer blocks. Most of the described block copolymers form micelles with either the more polar or the un-

polar block pointing outwards, i.e., regular or inverse micelles, depending on the solvent's polarity. Since we are interested in obtaining assemblies with chemical functionalities, a micelle morphology with the functional groups located in the micelle core is desired.

Table 18-1 summarizes some micelle sizes and their apparent polydispersities, as determined by dynamic light scattering. It must be underlined that the molecular weight and architecture are the same, since we started from the same, nearly symmetrical, parental polystyrene-polybutadiene block copolymer (PSB-II,  $M_{PS} = 44\,000$ ;  $M_{PB} = 21\,000$ ). It is seen that the swollen micelles usually exhibit diameters between  $50\text{ nm} < D_h < 200\text{ nm}$  with polydispersities of 5–30% Gaussian width.

Micelle formation is not restricted to solvents for polystyrene (here toluene). Micelles can also be inverted where the cholesterol substitution mediates dissolution in aliphatic hydrocarbons or the fluorinated blocks mediate dissolution in solvents with still lower cohesion energy (as expressed by the Hildebrandt parameter  $\delta$ ). Polar modification, on the other hand, results in solubil-

ity in methanol or water, as shown with the polyalcohol or polyacid substitution pattern.

Micelle formation can also be seen by electron microscopy. Figure 18-5 shows a typical picture characterizing these micelles; due to the lack of contrast the sample was shadowed with Pt/C.

The spherical shape of the micelles as well as their rather narrow size distribution are easily recognized. The difference between the diameter and the results of dynamic light scattering is due to the fact that DLS characterizes the micelles in a highly swollen state, whereas electron microscopy depicts the solid collapsed particles.

Similar experiments and static light scattering reveal that the size of these micelles is perfectly controlled by the length of the outer dissolved block ( $N_S$ ) and the core-forming block ( $N_C$ ), as well as the interface

**Table 18-1.** Micellar characteristics of the diverse amphiphilic block copolymers shown in Fig. 18-3. The hydrodynamic diameter  $d$  is determined by dynamic light scattering. The relative width  $\sigma$  of a Gaussian distribution is fitted to the relaxation curve and illustrates the polydispersity of the samples.

Solvent	Perfluoro(methyl-cyclohexane)	Hexane	Toluene	Methanol
$\delta [(\text{cal}/\text{cm}^3)^{1/2}]$	6.0	7.3	8.9	14.5
Polymer				
Alc-PSB-II	—	—	$d_h = 115.5\text{ nm};$ $\sigma = 0.059$	$d_h = 54.7\text{ nm};$ $\sigma = 0.265$
MP-PSB-II	—	—	$d_h = 153.0\text{ nm};$ $\sigma = 0.189$	$d_h = 48.0\text{ nm};$ $\sigma = 0.284$
MBT-PSB-II	—	—	$d_h = 208.2\text{ nm};$ $\sigma = 0.235$	—
Fluoro-PSB-II	$d_h = 111.8\text{ nm};$ $\sigma = 0.315$	—	$d_h = 176.1\text{ nm};$ $\sigma = 0.321$	—
Chol-PSB-II	—	$d_h = 58.6\text{ nm};$ $\sigma = 0.065$	—	—
Pht-PSB-II	—	—	$d_h = 97.4\text{ nm};$ $\sigma = 0.125$	$d_h = 50.8\text{ nm};$ $\sigma = 0.221$
Pyr-PSB-II	—	—	$d_h = 115.6\text{ nm};$ $\sigma = 0.387$	$d_h = 87.7\text{ nm};$ $\sigma = 0.343$





**Figure 18-5.** Electron micrograph of the micelles of a polystyrene-*b*-poly(4)vinylpyridine block copolymer contrasted with Pt/Ir. The high uniformity of these self-assembled structures can be recognized. The different shades of gray are related to different layer thicknesses, i.e., monolayer, double layer, etc., of stable micelles.

energy between core and solvent. The relation between the aggregation number  $Z$  and these quantities for the limit of high interface energies is given by (Antonietti et al., 1994; Förster et al., 1996)

$$Z = Z_0 N_C^2 N_S^{-0.8} \quad (18-1)$$

$$Z = 36\pi \left( \frac{V_m^2}{A_m^3} \right) \quad (18-2)$$

The quantity  $Z_0$  contains all geometric characteristics (the monomer volume  $V_m$  and the stabilized interface area per molecule  $A_m$ ) and is defined analogous to the surfactant ratio of low molecular weight surfactants. It was shown that these relations hold for chemically very different systems, such as nonionic surfactants and charged block copolymers.

With the presented terminology of the modular approach, these micelles can be regarded as the molecular base for a chemical system with the single polymer being the structural module forming well-defined and controllable spherical superstructures by

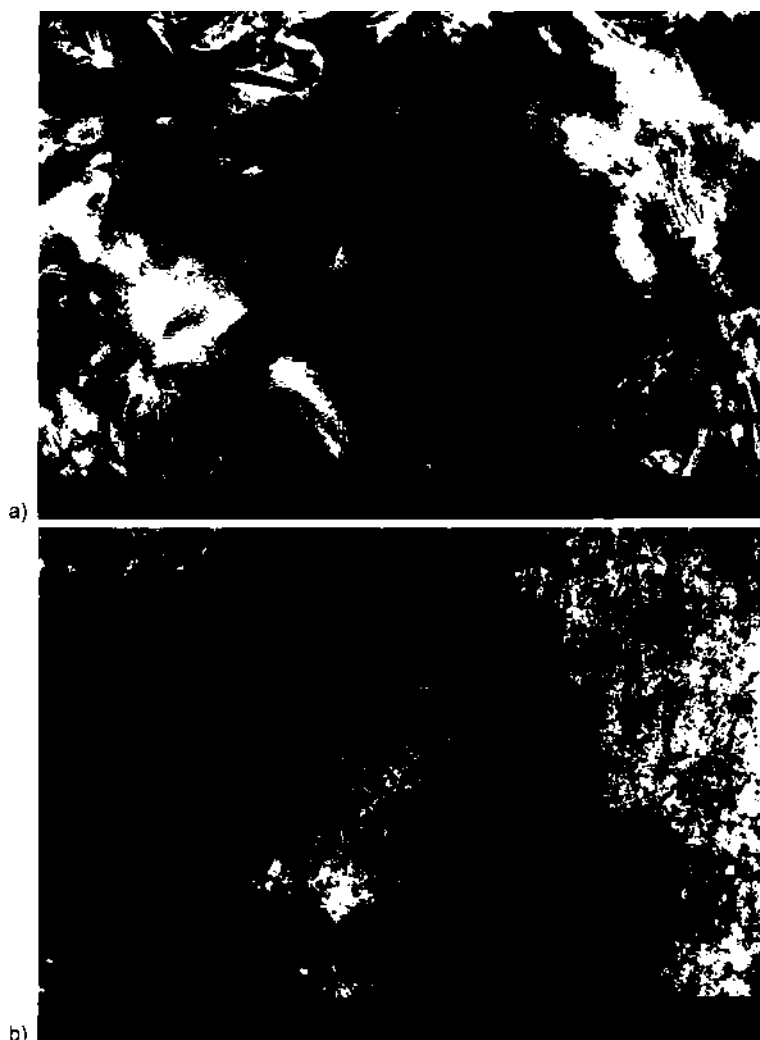
self-assembly and containing a highly functionalized micelle core, which is constructed to incorporate other components.

### 18.3.3 Solid State Properties and Liquid-Crystalline Phases of ABCs

ABC block copolymers form not only micelles in solution but also ordered mesophases in semiconcentrated solution or in the bulk. Phase formation occurs corresponding to standard block copolymers (Bates et al., 1994; Khandpur et al., 1995), where the relatively high interfacial energy results in the appearance of additional mesophases and phase effects (Oestreich et al., 1997).

The very high degree of order has already been seen by polarization microscopy. Figure 18-6 a and b show some textures for blocks modified with cholesterol tails (Fig. 18-6 a) and perfluorinated tails (Fig. 18-6 b).

The cholesterol-containing blocks show a typical thermotropic liquid crystalline texture, i.e., these polymers not only show mi-



**Figure 18-6.** a) Polarization micrograph of Chol-PSB-II. b) Polarization micrograph of Fluoro-PSB-II.

crophase separation due to the block copolymer structure, but the cholesteryl-containing microphase is liquid-crystalline in itself. DSC measurements reveal a nematic–isotropic transition of  $T_c = 203^\circ\text{C}$ . This value is within the data range of Fischer and co-workers (Arnold et al., 1994; Fischer and Poser, 1996), where similar liquid-crystalline block copolymers were synthesized via classical anionic polymerization including protecting group chemistry and subsequent esterification with a spaced cholesterol unit.

Clearly, the modular approach towards such systems producing polymers with very similar properties has the advantage of being simpler. It must be underlined that such ABCs with a functionality of being liquid-crystalline can also be used as stabilizers for the dispersion of liquid crystals in a continuous polymer, thus resulting in more stable polymer dispersed liquid crystals (PDLCs) with better morphology control.

Fluorinated ABC shows the appearance of strong colors in polarization microscopy,

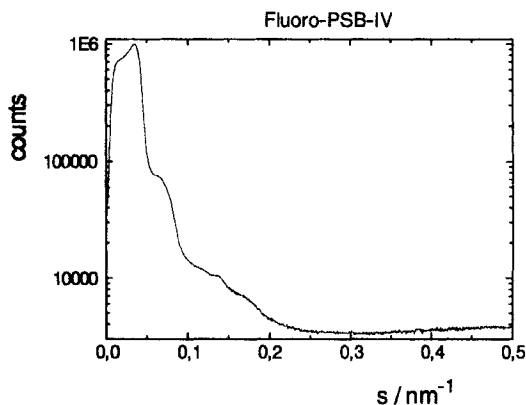
thus proving the very high spontaneous order and anisotropy of the samples (Fig. 18-6b).

The presented fluorinated ABCs are elastic, soft materials. DSC (differential scanning calorimetry) measurements and wide angle X-ray scattering (WAXS) diffractograms reveal the absence of side chain crystallinity of the fluorinated tails. With DSC we obtain a heating curve characterized by two glass transition temperatures, where the glass transition of the fluorinated phase  $T_g^1 = -25^\circ\text{C}$  and the glass transition of the polystyrene phase  $T_g^2 = 103^\circ\text{C}$ . These glass transitions have to be regarded as the limiting values for high molecular weights; smaller chains exhibit the typical depression of the glass transition temperature.

Fluorinated triblock copolymers with two terminal polystyrene blocks, which have also been synthesized (Oestreich et al., 1997) are (at room temperature) thermoplastic elastomers with a soft polymer phase (fluorinated block) and a hard phase (PS block), such as the parental polystyrene-*b*-polybutadiene block copolymer. Depending on the relative volume fraction of both components and the continuity of the phases, the resulting bulk material is a rubber or a high impact solid.

The high degree of order in the solid state of all these systems is backed by small angle X-ray scattering, where narrow peaks and unconventional peak sequences are obtained. An exemplary diffractogram is shown in Fig. 18-7.

Usually such phases consist of a simple fundamental symmetry and localized undulations on top of it; the interested reader is referred to Oestreich et al. (1997), where a structure assignment of this and similar polymers is given. In the present context, it is important that highly amphiphilic block copolymers form mesophases of high symmetry and order, where each microphase can



**Figure 18-7.** A small-angle X-ray (SAXS) diffractogram of Fluoro-PSB-IV. Unlike Fluoro-PSB-II, Fluoro-PSB-IV has a shorter polymer chain ( $N_{\text{PS}} = 106$ ,  $N_{\text{Fluoro}} = 34$ ), which adjusts the structure to be sufficiently small to be characterized by SAXS.

be designed to be highly functionalized and is able to incorporate other components. This is analogous to the chemistry in the micelle core and can be regarded as the solid film equivalent of the described “mother-board”.

Consequently, all the modifications described below, performed for simplicity in micelles, can, in principle, also be carried out in solid films, thus directly resulting in well-defined, three-dimensional arrangements of the functionalities.

### 18.3.4 Fluorinated Block Copolymers for Hydrophobic Coatings and Membranes, and as Dispersion Stabilizers

Besides the very interesting solid state structure, the fluorinated blocks have some interesting extra features which make them valuable materials.

As a result of the very low cohesion energy of their fluorinated part, the interfacial energy of these blocks to other media with a low cohesion energy is low; towards gases (with a cohesion energy close to zero), a

low surface tension  $\gamma$  is obtained. A minimized  $\gamma$ -value is important for the stability of foams with a fine foam structure. Surface energies smaller than 20 mN/m are called "ultra-low", since most standard solvents such as oil and water cannot wet such surfaces; their importance for protective and nonpolluting coatings, water repelling fabrics, or self-lubricating machine parts have already been discussed in the literature (Schmidt et al., 1994, 1996). The nonsticky "standard" polymer, PTFE, exhibits a  $\gamma$ -value of 18.6 mN/m, but has the disadvantages of being difficult to process and having a porous surface.

Since it is well known that the polymer/air interface severely influences and orients the phase structure of block copolymers, we expect that in close proximity to the surface the component with the lower cohesion energy density is remarkably enriched. It was shown with polystyrene-*b*-PDMS block copolymers that the doping of a bulk material (in this special case, polystyrene) with blocks enables significant lowering of the surface energies due to this enrichment (Chen and Gardella, 1994).

The same is true for the fluorinated ABCs discussed here: They exhibit a  $\gamma$ -value well below that of PTFE as measured by the contact angle towards hexadecane (Oestreich et al., 1997). Contrary to PTFE, the blocky nature of the polymer presented here enables thermoplastic processing and dissolution in standard solvents, ensures adhesion towards the substrate, and possesses a planar surface structure, which are beneficial for practical applications.

A related interface problem with high technological impact in which fluorinated ABCs are successfully applied is the stabilization of standard polymers and in solvents with very low cohesion energy, such as short chain hydrocarbons (isopentane, butane, propane), fluorinated solvents, and super-

critical CO<sub>2</sub>. DeSimone and co-workers showed that heterophase polymerization in supercritical CO<sub>2</sub> enables the solvent-free synthesis of polymer powders with excellent handling of the polymerization process (DeSimone and Guan, 1994; DeSimone et al., 1994). Since most polymers do not dissolve in CO<sub>2</sub>, they precipitate during the polymerization and steric stabilizers are required to keep the dispersed state. This problem is classically attacked via copolymerization with fluoroalkylmethacrylates or the addition of fluorinated surfactant, both being weak steric stabilizers. In a recent paper, DeSimone et al. (1996) also applied a fluorinated block copolymer, proving the superb stabilization efficiency of such systems via a rather low particle size.

Testing of our fluorinated block copolymers as steric stabilizers in low cohesion energy solvents was performed on the basis of the precipitation polymerization of styrene in Freon 113, a model for the technologically more relevant case of polymerization in dense CO<sub>2</sub>. Table 18-2 gives the colloid analytical data of some of the final latex dispersions.

It is seen that the fluorinated ABCs (as expected) stabilize the dispersions with relatively low amounts of stabilizers: The addition of only 5 wt.% enables the synthesis

**Table 18-2.** Results of precipitation polymerization of polystyrene in solvents with low cohesion energy density, here Freon 113 with Fluoro-PSB-IV as a steric stabilizer. The resulting particle diameter  $d_h$  and the resulting Gaussian width  $\sigma$  are given based on the relative amount of surfactant, which varies between 5 and 20 wt.% with respect to monomer.

$S = [\text{Fluor-PSB-IV}]/[\text{styrene}]$	$d_h(\text{nm})$	$\sigma$
0.05	244.7	0.341
0.10	189.9	0.186
0.20	107.1	0.212

of latex particles with a diameter of 250 nm, which can be rated as a very fine size for a precipitation polymerization with steric stabilization.

The preference of the fluorinated tails to gases can be exploited in a third way: Perfluorinated alkanes are known for their remarkable inclination for oxygen (Riess, 1995), and polymeric gas membranes containing ultra-hydrophobic moieties show high selectivity in gas separation, e.g., in the O<sub>2</sub>/N<sub>2</sub> separation process (Österreich, Antonietti, to be published). For these reasons, some preliminary gas permeation measurements were performed on thin layers of a fluorinated ABC spun on porous polypropylene supports. Since analysis of the effective flow geometry of such systems is rather complicated, only relative values of the permeability are presented in Table 18-3 [taken from Oestreich et al. (1997)].

**Table 18-3.** Results of gas permeation measurements on porous cellgard membranes coated with thin films of Fluoro-PSB-II and Fluor-Kraton<sup>a</sup>. In the case of Fluor-Kraton, we modify a commercially available polystyrene-*b*-polybutadiene-*b*-polystyrene triblock copolymer. It is seen that both systems exhibit a remarkable enrichment of CO<sub>2</sub> or O<sub>2</sub>, respectively, at comparably high permeabilities.

	Flow (cm <sup>3</sup> /min)	CO <sub>2</sub> (%)	CH <sub>4</sub> (%)	C <sub>2</sub> H <sub>4</sub> (%)
Feed	10	20	40	40
Fluoro-PSB-II	1.2–2.0	43.6	25.1	31.3
Fluoro-Kraton	2.8–5.6	37.5	29.2	33.2

	Flow (cm <sup>3</sup> /min)	O <sub>2</sub> (%)	N <sub>2</sub> (%)
Feed	10	20	80
Fluoro-PSB-II	0.6	28.5	71.5
Fluoro-Kraton	1.4	27.1	72.9

<sup>a</sup> At room temperature,  $p = 5$  bar ( $5 \times 10^5$  N m<sup>-2</sup>) for 3 h.

Both for the separation of CO<sub>2</sub> from gaseous hydrocarbons as well as for oxygen from nitrogen, a comparably good selectivity at a rather high flow rate is obtained. This underlines the advantages of a thermoplastic ABC with a self-organized microphase structure which consists of a continuous liquid transport phase within the frame of a supporting solid polymer phase for the construction of very effective membranes. The full profit of the modular conception, however, will arise from the incorporation of additional selectivity or solubility enhancing components.

### 18.3.5 Amphiphilic Block Copolymers that take up Metals and Semiconductors

As described above, ABCs can be made to exhibit a substitution pattern based on ligand molecules, which enables the binding and uptake of metal salts into organic solvents. In other words: Such micellar solutions of the block copolymers readily solubilize different metal salts which are otherwise insoluble in the solvent. This kind of solvation power is a typical property of ABC micelles and might also be used for applications such as the generalized phase transfer catalysis of drug formulation.

To delineate some “modular chemistry” ideas in polymer synthesis, these metal salt-containing micelles with their high kinetic and thermodynamic stability were employed as “molecular reactors” by transfer of the dissolved metal salts to metal colloids of uniform size in the nanometer region. This route is currently being developed and optimized by a number of research groups (Moffitt and Eisenberg, 1995; Ng Cheong Chan et al., 1992; Yue and Cohen, 1994; Saito et al., 1992; Roescher and Möller, 1995 a, b; Antonietti and Heinz, 1992; Antonietti et al., 1995) to produce materials combining inorganic as well as polymer properties.

Usually the micelles depicted above change their colloidal properties (such as size) only slightly during solvation, which is due to the already high interfacial energy of the core. On the other hand, it is possible to induce micelle formation of weakly aggregating systems by the uptake of highly dipolar groups. It has also been observed that not all the substitution patterns in the metallophilic ABCs are equally well suited for all salts (Antonietti et al., 1996a). The data seem to follow the hard–soft acid–base principle, where “soft” cations require “soft” ligands, whereas “hard” cations show a distinct affinity to “hard” ligands.

The subsequent conversion of the metal salts, e.g., via reduction or via oxidic or sulfidic precipitation, produces the desired metal colloids or semiconductor particles inside the micelle core. In the case of a slow and homogeneous reaction and slow nucleation, it is possible to convert all the metal ions of one micelle core to one colloid particle, the size of which is controlled only by the micelle size and the relative metal content.

This situation with its “cherry” morphology is shown in Fig. 18-8a (Antonietti et al., 1995). Such an architecture is profitable for incorporating colloidal modules with definite magnetic, optic, or electronic properties.

In the case of a fast homogeneous reaction, many colloids per micelle are usually nucleated, and we obtain a structure that is called a “raspberry” morphology (Antonietti et al., 1995), as shown in Fig. 18-8a. Here the very small colloidal particles are effectively stabilized in the micelle. As a result of their enormous surface of up to  $1000 \text{ m}^2/\text{cm}^3$ , this architecture is advantageous for catalytic applications of these material hybrids.

The scenario of a heterogenous reaction (which is the third case) becomes complex

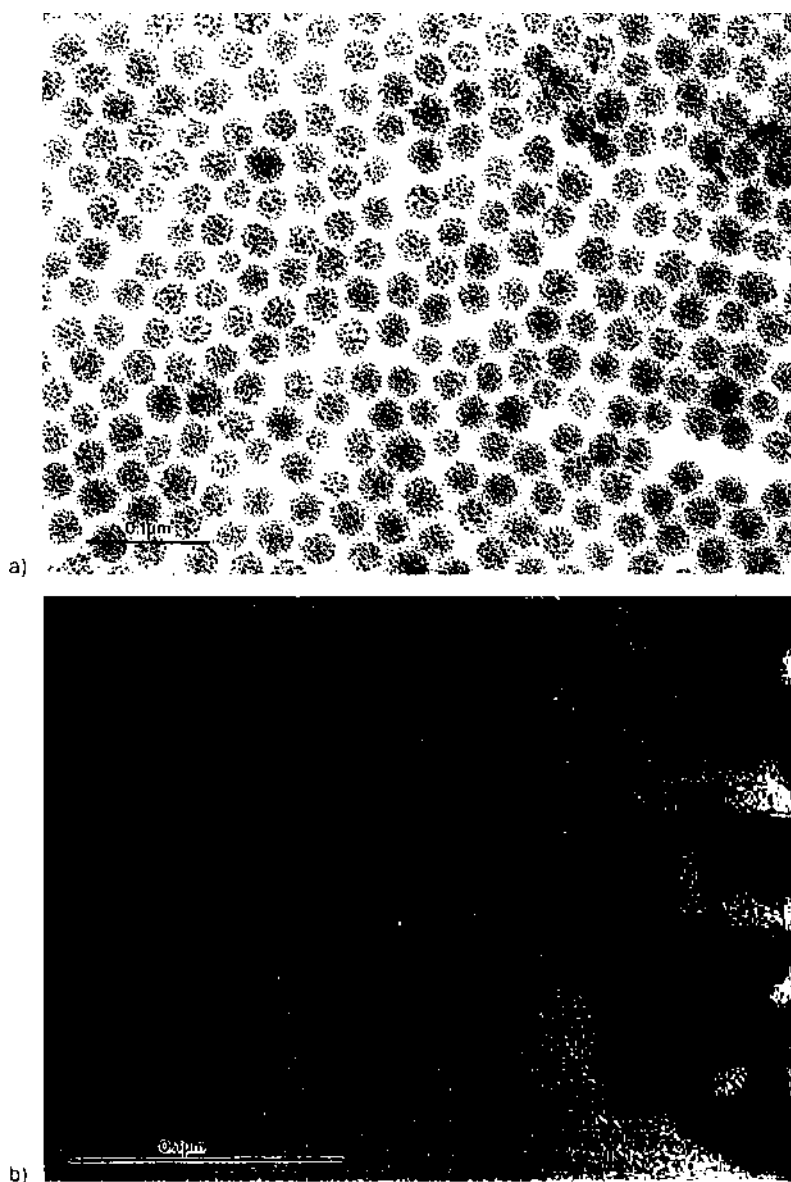
and is not directly controlled by the micelles. For the formation of gold colloids, it was shown that even aubergine-shaped particles are formed in the early phases of the reaction, which is seen as a typical double plasmon resonance in the UV–vis spectrum (Antonietti et al., 1996b). The proceeding interface reaction breaks up the micelles, which, however, return to stabilize the final colloid particles when the colloid leaves the reaction center.

It must be underlined that the solvent can be completely removed from all our colloidal solutions, thus resulting in solvent-cast polymeric films with additional properties of the metal colloids. This process is completely reversible: The solid films can be redissolved in all solvents for polystyrene without any significant change of the colloidal characteristics, thus proving the close-to-perfect stabilization of the metal colloids by the block copolymer shells.

The control of magnetic properties via particle morphology and size was successfully shown by control of the morphology of cobalt colloids within block copolymer micelles (Platonova et al., 1997). Here the whole transition from paramagnetic through superparamagnetic to ferromagnetic behavior was obtained, depending on the type of block copolymer and the reaction conditions. At the same time, the magnetic fluids thus constructed exhibit a high absolute value of magnetization.

The control and installation of special optical properties was obtained by means of the synthesis of ZnO colloids in polymer films where the semiconductor ZnO acts as a UV absorber, cutting the complete frequency range with  $\lambda < 350 \text{ nm}$  (Antonietti et al., 1996c). Here the modular hybrid can replace the standard organic UV absorbers with their known disadvantages.

A first testing of the catalytic activity of the palladium colloids with raspberry



**Figure 18-8.** a, b) Transmission electron micrographs of different morphologies of noble metal colloids in block copolymer micelles: a) the "raspberry" morphology containing many metal colloids per micelle core, and b) the "cherry" morphology containing only one colloid per particle. The micelles are visible as shadows or a background texture.

morphology, stabilized with polystyrene-*b*-poly(4)vinylpyridine block copolymers, showed in hydrogenation reactions an increased stability and selectivity at a level of reactivity that is about comparable to optimized industrial reference systems (Antonietti et al., 1995; Seregina et al., 1997). These observations are backed by newer re-

sults, where these colloids were employed in the Heck reaction (palladium- or nickel-catalyzed C–C coupling) (Klingelhöfer et al., 1997). In all cases the reactivity was slightly reduced, but the lifetime of the catalysts exceeded the corresponding ones of low molecular weight catalysts by orders of magnitude (turnover numbers > 20 000).

During testing in catalytical applications, we also performed experiments in cyclohexane which is a  $\theta$ -solvent for the solvating polystyrene blocks. The switch between a stable colloidal solution at elevated temperatures and a colloidal gel phase at  $T < 308$  K is fully reversible and allows very simple separation of the reaction products and the polymer-supported colloidal catalyst by cooling; this catalyst can be reused in the next reaction cycle in the same reaction vessel without any loss and long-winded isolation procedures. This is a clear extra advantage which is brought into the system by the stabilizing block copolymer module.

All these points underline the advantages of a modular concept for such catalysts. The reactivity is brought in by the colloidal noble metal module, whereas stability, (switchable) solubility, and selectivity arise from the polymeric stabilizers. The systems tested first still had the disadvantage that only one metal binding site (the pyridine unit of the P4VP blocks) per monomer unit was available and that the electronic characteristics of this substituent are fixed. As shown above, modular synthesis of such metal-binding block copolymers enables the synthesis of a variety of different structures, such as chelating ligands, an adjustable polarizability, and an adjustable electronic influencing or an improved amphiphilicity (in the general sense). Since optical and electronic properties (Lewis, 1993; Henglein, 1989; Weller, 1993), as well as the catalytic activities, react sensitively to the dielectric environment and donor/acceptor groups, we expect the properties of the embedded colloid to be fine-tuned by the surrounding ABCs. Experimental confirmation of these possibilities, however, has to be established.

## 18.4 Conclusions and Outlook

It was demonstrated that the decoupling of the build up of chain length and architecture of a polymer molecule, on the one hand, and design of the chemical functionality by polymer-analogous reactions, on the other, yield a whole variety of highly valuable amphiphilic block copolymers with a broad spread of “amphiphilicity” and related functions.

Most of these ABCs are interesting in themselves, since they are able to stabilize the interfaces between very different media, such as polymers, metals, and gases. Within the framework of supramolecular and modular chemistry, these molecules act as “connectors”, i.e., as molecular glues between other diverse subunits. Typical examples for these applications are ABCs with a fluorinated block or a liquid-crystalline block, which are mainly interesting as special dispersion stabilizers or surface modifiers.

By the means of some selected ABCs, it was shown that modification with metallophilic or ionophilic binding moduli (containing complexing or highly dipolar substituents in the chemical structure) results in polymers that effectively stabilize nano-sized metal or semiconductor colloids. In this case, the resulting polymer/metal or polymer/semiconductor hybrids can be regarded as real modular chemical systems, since they offer a unique combination of polymeric properties (stability, elasticity, and processability) with those of the metal or semiconductor colloids (optical, electronic and magnetic behavior, and catalysis). In addition, the outer shell of stabilizing blocks directly allows a colloiddally dispersed incorporation in a polymer film or a switchable solubility, i.e., it is still possible to define/program the molecular interface to other systems.



Since the presented modular scheme is rather general, the working principle even for the synthesis of ABCs is far from exploited and offers some additional perspectives. It is straightforward, for instance, to couple as the first step the parental block copolymer module with larger molecular objects with multifunctionality from other sources, e.g., proteins or oligosaccharides (via their end groups). This may result in new material hybrids and the design of new, near-biological interfaces. Another very promising area is modification or multigrafting with oligomers or shape-persistent molecules, which might result in a more generalized structural layout of new block copolymer phases and solid state morphologies.

Considering also the beauty of the resulting structures and the simplicity of the modular approach, further developments in the design of functional modules employing amphiphilic block copolymers will be interesting to follow.

## 18.5 Acknowledgements

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## 19 Synthesis of Cyclic Macromolecules

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## List of Symbols and Abbreviations

$C_{eq}$	concentration at which cyclic and linear structures are formed with the same probability
$D$	translational diffusion coefficient
$K_x$	equilibrium constant
$M$	molar mass
$M_e$	entanglement molar mass
$N_A$	Avogadro number
$P$	probability
$P_{intra}, P_{inter}$	probability of intramolecular/intermolecular reaction
$\langle r^2 \rangle$	mean square end-to-end distance of a Gaussian chain
$R_g$	radius of gyration
$T_g$	glass transition temperature
$x, y$	number of monomer units
$\tau$	volume element
BIPE	bis(isopropenyl-4-phenyl)ethane
Bu	butyl
D <sub>3</sub>	hexamethylcyclotrisiloxane
D <sub>4</sub>	2,4,6,8-tetramethylcyclotetrasiloxane
DNA	deoxyribonucleic acid
DPE	1,1-diphenylethylene
DP <sub>n</sub>	number degree of polymerization
1,3-DXL	1,3-dioxolane
Me	methyl
PB	polybutadiene
PCEVE	poly(2-chloroethyl vinyl ether)
PDMS	poly(dimethylsiloxane)
PDXL	poly(1,3-dioxolane)
PEO	poly(ethylene oxide)
PI	poly(isoprene)
PS	poly(styrene)
P2VP	poly(2-vinylpyridine)
SANS	small angle neutron scattering
SEC	size exclusion chromatography
Sty	styrene
THF	tetrahydrofuran
UV	ultraviolet
2VP	2-vinylpyridine

## 19.1 Introduction

The synthesis of tailor-made polymers is a major challenge for polymer chemists (Gnanou, 1996; Rempp et al., 1994). There has been increasing interest in cyclic oligomers or polymers over the years with special attention on macrocyclic polymers since the early 1950s. Theoretical calculations of the cyclization effect on the solution behavior and the solid state properties of cyclic macromolecules, as compared to the linear equivalent, were dealt with in a number of papers: Zimm and Stockmayer (1949), Bloomfield and Zimm (1966), Casassa (1965), Burchard and Schmitt (1980), Ten Brinke and Hadziioannou (1987), and Kosmas et al. (1994). As an example, the mean square radius of gyration of a cyclic polymer in a theta solvent or in the bulk should be exactly half that of the linear molecule exhibiting the same molar mass (Casassa, 1965). The absence of chain ends is also expected to have consequences on the properties in the solid state: The glass transition temperature ( $T_g$ ) decreases for linear chains with decreasing molar mass. As theoretically discussed by DiMarzio and Guttman (1987), this should not be the case for cyclic structures. The driving force for the development of efficient preparation methods of well-defined cyclic polymers in a large domain of molar masses was directly connected to the problem of reptation of polymers: can a cyclic polymer reptate in the same way as a linear chain? Is the reptation affected by the molar mass? The concept of reptation was first developed for linear chains many years ago by Edwards (1967) and De Gennes (1971). More recently, Klein (1986) has theoretically examined the dynamics of entangled linear, branched, and cyclic polymers on the base of this reptation concept.

Comparison between the experimental results and the theoretical predictions has only been possible since around 15 years ago, when well-defined cyclic polymers were available in rather large quantities. It has to be mentioned that cyclic structures already existed in biological molecules such as DNA (Freifelder et al., 1964, Cantor and Schimmel, 1979). The existence of twisted DNA structures was demonstrated by Crawford (1965).

The synthesis and properties of cyclic polymers have been discussed over the years in several review articles (Deffieux, 1996; Ma, 1996; Rempp et al., 1987; Semlyen, 1976, 1997). The purpose of the present work is to present the state-of-art in this domain.

The first part of this work deals with the application of ring-chain equilibria to the preparation of cyclic polymers involving back-biting reactions. This procedure does not allow the synthesis of cyclic polymers and linear precursor of the same molar mass, and the domain of accessible molar masses is limited. This is why many efforts have been devoted to the search for efficient end-to-end cyclization procedures to synthesize homopolymeric cycles of controlled molar mass. This latter aspect will be extensively discussed in the second part of the text, together with the preparation of cyclic species exhibiting block copolymeric chains. These end-to-end cyclizations of  $\alpha, \omega$ -living polymers with bifunctional compounds have their own limitation. Therefore the advantage of cyclization reactions, where the end groups of heterofunctional polymers are linked together, will be discussed in detail.

All the samples obtained, either by ring-chain equilibria or end-to-end cyclization have to be characterized properly to confirm the expected cyclic structure. In most cases, they have to be isolated first from the raw reaction product. They were used in sever-

al studies from semi-dilute solution to solid state. These different properties will be discussed in the second part.

Over the years there has been rising interest in structures derived from cyclic polymers. The different cyclization reactions previously discussed could be extended to the preparation of novel architectures, such as eight-shaped polymers, rotaxanes, polyrotaxanes, and similar species, which will be briefly presented in Secs. 19.4.1 and 19.4.2.

## 19.2 Synthesis of Cyclic Structures

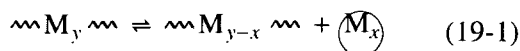
The synthesis of cyclic polymers can be achieved in two different ways, either by ring-chain equilibria reactions or by end-to-end cyclization reactions of polymers obtained by ionic polymerization.

### 19.2.1 Ring-Chain Equilibria and Cyclization

Polymers based on vinylic or dienic monomers are generally obtained by free-radical polymerization or ionic polymerization processes free of any cyclic constituents. In these polymers, no reactive functions are located along the chain which may induce cyclization reactions. This is not the case for polymers obtained by polycondensation (polyesters, polyamides, etc.) or for polymers based on heterocyclic monomers. Both reactions have been extensively studied over the years. Depending upon the experimental conditions, they mostly provide access to the linear polycondensate or polymer, or to a mixture of linear polymer and more or less significant amounts of cyclic species. The reaction of a function located at the chain ends with a functional link along the chain is responsible for cyclization. In

most cases, these cyclic polymers are considered as undesirable side products, and the experimental conditions are adjusted to limit their formation. For example, high concentration or bulk polymerization is applied to disfavor cyclization by intramolecular reaction (back-biting) (Scheme 19-1). The number of macromolecules formed increases in relation to the decrease of their average molar mass. If this reaction occurs intermolecularly (scrambling), cyclic structures do not result, but there is a broadening of the molar mass distribution.

The probability of the formation of cyclic structures can be calculated from Jacobson and Stockmayer (1950) theory, first applied to step-growth polymerization in the bulk. The formation of a cyclic  $x$ -mer is presented below



where  $M_y$  refers to a linear chain with  $y$  monomer units and  $M_x$  to a cyclic polymer with  $x$  monomer units

The equilibrium constant  $K_x$  can be expressed

$$K_x = \frac{[\sim M_{y-x} \sim][\textcircled{M_x}]}{[\sim M_y \sim]} = \frac{[\textcircled{M_x}]}{p^x} \quad (19-2)$$

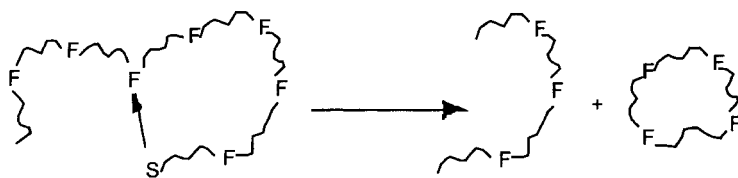
with  $p$  being the probability for the functions having undergone reaction. Provided the polymer chains obey Gaussian statistics, the equilibrium constant relates to the probability of chains with  $y$  monomers having their chain ends overlapping

$$K_x = \left( \frac{3}{2 \pi \langle r_x^2 \rangle} \right)^{3/2} \frac{1}{2 N_A x} \quad (19-3)$$

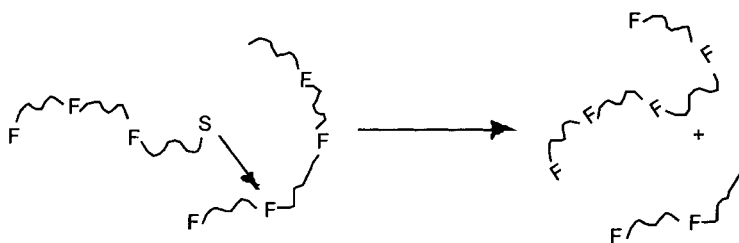
where  $N_A$  is the Avogadro number,  $\langle r^2 \rangle$  is the mean square end-to-end distance of a Gaussian chain.

As just mentioned, beside the cyclization reaction occurring in chain extension reac-

a) Intramolecular reaction: back-biting



b) Intermolecular reaction: scrambling



F: ester function, siloxane bridge, ester bridge, ...

S: alkoxide, silanolate function, oxonium site, ...

**Scheme 19-1.** Schematic representation of the synthesis of cyclic structures via ring chain equilibria reactions.

tions, such as the transesterification of esters, cyclic structures also appear in some living cationic or anionic polymerization reactions (back-biting and end-biting) of heterocycles. In both cases, cyclic structures can be formed during the polymerization or the polycondensation process, or upon reaction of a linear polymer with an appropriate reagent. It is also necessary to be aware of the fact that, in most cases, the molar masses of cycles formed under such conditions are rather low and the molar mass distributions large. The purpose of the present work is not to discuss all the examples. Only the most important or most promising examples will be presented. The preparation and isolation of cyclic poly(dimethylsiloxane)s (PDMSs) will be discussed first. These species have been extensively studied over the years, with special emphasis on the synthesis of well-defined high molar masses cyclic PDMS. Examples of cyclic structures in various heterocycles, such as cyclic ethers

including acetals based essentially upon cationic polymerization, will be given. Finally, some cases of cyclic structures in polyesters or polyamides will be discussed.

### 19.2.1.1 Ring-Chain Equilibria in Siloxane Heterocycles

Brown and Slusarczuk (1965) were the first to report on the existence of macrocyclic populations in PDMS. Upon heating, hexamethylcyclotrisiloxane ( $D_3$ ) or 2,4,6,8-tetramethylcyclotetrasiloxane ( $D_4$ ) in the presence of potassium hydroxide, either diluted or not, yields access to PDMS containing linear polymer and cyclic species. By using appropriate separation methods, such as gas-liquid chromatography, size exclusion chromatography (SEC), and fractional precipitation, they succeeded in isolating from the raw reaction product the linear polymer and the different cyclic constituents. Even if these different cyclic species



could only be obtained in rather low amounts and for low molar masses, a comparative study of the dependence of the experimental molar cyclization constant versus the number of siloxane units to the theoretical calculation could be achieved.

The first systematic investigation to prepare high molar mass, cyclic PDMS was performed by Dodgson and Semlyen (1977), who reported the preparation, isolation, and characterization of cyclic PDMS. As expected from Jacobson and Stockmayer calculations, the probability of cyclization decreases as the dimension of the chain increases. The molar mass distributions for a given fraction are still large. They thus developed efficient separation techniques based on SEC and were able to isolate, from the raw reaction product, PDMS fractions characterized by sharp molar mass distributions. PDMS with molar masses up to 30 000 g/mol were available. These samples were extensively studied from their solution properties to confirm the expected structure, and at higher concentrations from semi-dilute solutions to the solid state. This point will be discussed in the second part together with results on cyclic polystyrenes (PS) obtained by end-to-end cyclization reactions.

It was established a long time ago that the replacement in linear PDMS of the methyl by other substituents strongly modifies their properties (solution behavior, solid state properties, and crystallization) (Lewis, 1948; Harris et al., 1976). No systematic studies of the effect of the substituent's nature and the size of the cycle on these properties was published until the work of Clarson and Semlyen (1986). They could take advantage of their experience in the preparation and isolation of cyclic PDMS to synthesize cyclic poly(phenylmethylsiloxanes). Well-defined cyclic polymers covering a large domain of molar masses could be obtained and their properties were examined

in detail. The method, based on back-biting reactions, still has some limitations: Samples with molar masses higher than 30 000 g/mol cannot be obtained and this method does not enable the preparation, in the same synthesis, of cyclics and linear chains having exactly the same molar mass. In addition, ring-chain equilibria cannot be applied to the preparation of cyclic polymers based on vinylic monomers. Jones (1974) reported a few years ago on the preparation of cycles containing a more or less well-defined PDMS block and a central PS block. The PS sequence has been obtained by anionic polymerization, whereby the molar mass can be controlled in advance and molar mass distributions are narrow. The living chain ends are thus used after modification to introduce the PDMS sequence. A direct deactivation of these chain ends by efficient bifunctional deactivators may provide access to well-defined cyclic polymers. This aspect will be discussed in the second part of the text.

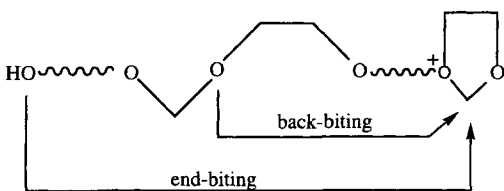
#### 19.2.1.2 Ring-Chain Equilibria in Other Heterocycles

The preparation of the cyclic PDMS just discussed referred to either anionic or cationic ring-opening polymerization of cyclosiloxanes. This ring-opening polymerization can be applied to many other heterocyclic monomers, providing access to polymers containing, beside the linear chains, more or less important quantities of cyclic oligomers of various dimensions. Only a few examples will be presented here. The size of cyclic polymers or oligomers based on heterocycles is directly related to the structure of the heterocycle itself. In some cases, as just discussed for PDMS, rather large cycles can be obtained in a controlled manner; in other cases, such as oxirane, the reaction seems to be strictly limited to the formation of cyclic dimers.

The anionic polymerization of ethylene oxide gives access to well-defined linear polymers: No cyclic materials are detected. If ethylene oxide is polymerized by boron-trifluoride in 1,2-dichloromethane (Latre-mouille et al., 1960), not only are the average molar masses limited to values around 700 g/mol, but also the nature itself of the polymer formed can be discussed. Some authors have claimed that 1,3-dioxolane is formed as well as the polymers (Worsfold and Eastham, 1957).

Cationic polymerization (or oligomerization) is a good example of reactions where the different factors influencing cyclic oligomer formation were studied in detail (Goethals, 1977). Other different epoxides, such as epichlorohydrin (Ito et al., 1979), have been found to give access to cyclic oligomers.

The formation of cyclic structures has also been examined in the cationic polymerization of cyclic 1,3-dioxolane (Scheme 19-2) or 1,3-dioxepane in the presence of various catalysts (Andrews and Semlyen, 1972). The presence of cyclic oligomers ( $DP_n$  from 2 to 9) was detected in these reactions, borontetrafluoride being used as the initiator and diethyl etherate as the catalyst. The molar equilibrium constant  $K_x$  was measured either in undiluted medium or in solution and the values were found to be in agreement, at least for  $x > 5$ , with the Jacobson–Stockmayer theory. The question as to whether the equilibrium occurs between cyclic monomer and cyclic polymer or cyclic monomer and chain polymer still remains



**Scheme 19-2.** Intramolecular cyclization in PDXL.

open. The presence of cyclic oligomers was also mentioned in tetrahydrofuran (THF) by McKenna et al. (1977) and in other five-, six-, or seven-membered cyclic ethers by Goethals (1977). The polymerization of heterocyclic monomers, especially 1,3-dioxolane, can also be conducted in the presence of oligomeric initiators such as  $\alpha$ -hydro- $\omega$ -hydroxypoly(ethylene oxide)s, where reaction products containing cyclic copolymeric oligomers can be obtained (Franta et al., 1990).

Along the same line, substituted thiiranes (Van Craeynest and Goethals, 1976; Goethals, 1977) and substituted aziridines (Dick, 1970; Goethals, 1977) have been found to produce cyclic oligomers when polymerized cationically. The following reaction scheme is generally admitted: For all substituted thiiranes, rapid polymerization is followed by degradation leading to the cyclic oligomers. With 1-alkylaziridine the mechanism seems more complicated.

The chemistry of cyclic oligomers is also more or less directly related to the synthesis of crown ethers, i.e., molecules that have the ability to bind one or two metal ions per cavity and to complex large organic cations (Lehn et al., 1988).

### 19.2.1.3 Cyclization Reactions in Polyesters or Polyamides

Upon heating a polyamide or a polyester in the presence of a transesterification or transamidification catalyst, the cyclization equilibrium may be reached. Over the years, various cyclic polyesters have been obtained, as has been reported by Semlyen (1986), Hubbard et al. (1996), Bryant and Semlyen (1997), Hamilton and Semlyen (1997), and Wood et al. (1997). As demonstrated by Semlyen in earlier experiments, the ring-chain equilibria reaction conducted either on aliphatic esters or in undiluted

medium only provided access to cyclic oligomers esters with a limited number of units in the cycle. Thus cyclic and linear constituents are present in the medium. As for cyclic PDMS, the proportion of cyclic species depends on the concentration, as dilution favors intramolecular over intermolecular reactions.

The presence of cyclic oligomers in polyamids has been established since the early work of Carothers (1937) on aliphatic polyamides. The extent of cyclic oligomers is generally low, because the polycondensation reaction is usually conducted in the melt where the formation of a cyclic structure has been shown by Jacobson and Stockmayer to be unfavorable. Furthermore, due to the rather limited molar masses of these cyclic oligomers, cyclic aliphatic polyamides have only attracted limited interest. On the other hand, special interest has recently been devoted to the synthesis and study of cyclic aramids. This class of polyamides (polyarylamids) is characterized by the presence of only aromatics units in the main chain, whereby a very high thermooxydative stability is reached. In addition, linear polyaramids, due to the inflexibility of the extended chain, give access to highly crystalline materials. The effect of cyclization on the crystalline properties of these rigid materials, i.e., the possibility of preparing such cyclics, has been discussed in detail by Memeger (1996) in a review article. It is necessary to be aware of the fact that the first generation of cyclic oligomers, i.e., the cyclic corresponding to the linear aramid (*p*-phenylene terephthalamide), cannot be obtained. As an example, macrocyclic aramids (Fig. 19-1) were obtained in good yields by reaction of *N,N'*-diisobutyl *para*-phenylene diamine with terephthaloyl chloride at elevated temperature and high dilution. As reported by Memeger, the use of the classical ring expansion reaction in oligo-

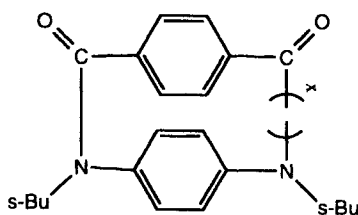


Figure 19-1. Cyclic poly(aramids)

cyclic polyaryamides has also been examined. This reaction provides access to linear aramids.

For many industrial applications in the melt, cyclic oligomers of poly(ether sulfones), characterized by their reduced viscosity as compared to the linear precursor, are of special interest for their potential to provide direct access to the linear homologs by ring-opening polymerization. Poly(ether sulfone) cycles are well known to generally contain, beside the linear polymer, more or less significant quantities of cyclic structures of various dimensions, and are generally limited to low molar masses. This constitutes a major drawback, as this linear chain may also be involved in the ring-opening polymerization of the cyclics. Xie and Gibson (1996) have succeeded in the synthesis of a 40-member cyclic arylene ether sulfone with a rather satisfactory cyclization yield. The availability of well-defined cyclic oligomers opens new perspectives in the synthesis of alternative copolymers.

Polycarbonates based on bisphenol A and obtained by interfacial polymerization have also been investigated (Horbach et al., 1980). Saponification reactions confirmed the presence of cyclic species.

### 19.2.2 End-to-End Cyclization Reactions

It is now well established that the most appropriate methods to synthesize tailor-

made macromolecules are based on ionic polymerization. Neither transfer nor termination reactions occur. This polymerization method allows predetermination of the molar mass and a narrow molar mass distribution. The presence of active sites at the chain ends provides access to a large scope of functionalization reactions. This method is especially useful for synthesizing well-defined cyclic structures, which, as an additional advantage, can be obtained together with their linear analogs in the same reaction. This is of special importance; the linear material is often used as a reference in all the characterization studies. As in ring-chain equilibria reactions, the concentration at which the cyclization reaction is conducted is decisive for reaching high cyclization yields. The synthesis of cyclic polymers by end-to-end cyclization refers to a process where the intramolecular reaction (cyclization) and the intermolecular reaction (linear growth) occur simultaneously. The concentration ( $c_{eq.}$ ) at which cyclic and linear structures are formed with the same probability has been calculated for irreversible cyclization by Hild et al. (1980) according to the Jacobson–Stockmayer theory. The first approximation found that all functions exhibit the same reactivity and no deactivation occurs. The probability of intramolecular reaction ( $p_{intra}$ ) depends on the concentration and the molar mass of the precursor polymer. The behavior of the chain is supposedly Gaussian and the probability of cyclization is determined by the probability for the two chain ends to be in immediate vicinity of each other, within the same volume element  $\tau$

$$p_{intra} = \frac{c}{M} N_A V \tau \left( \frac{3}{2\pi \langle r_x^2 \rangle} \right)^{3/2} \quad (19-4)$$

where  $N_A$  is the Avogadro number and  $\langle r^2 \rangle$  the mean square end-to-end distance of the precursor polymer.

The probability for intermolecular reaction  $p_{inter}$  can be calculated by

$$p_{inter} = \frac{1}{3} \frac{c^2}{M^2} N_A^2 V \tau \quad (19-5)$$

The concentration at which both reactions occur with the same probability is given by

$$c_{eq.} = 3 \left( \frac{3}{2\pi} \right)^{3/2} \frac{M}{(\langle r_x^2 \rangle)^{3/2}} \frac{1}{N_A} \quad (19-6)$$

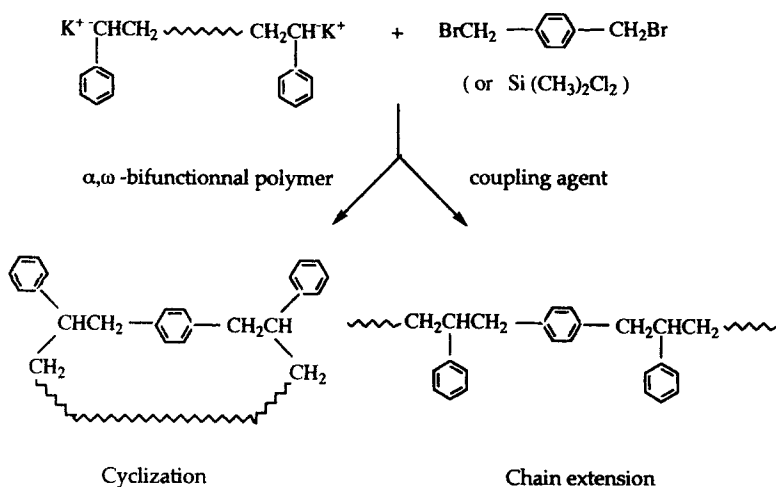
To reach high cyclization yields, the reaction has to be conducted far below this concentration.

The complexity of the kinetic behavior of this reaction was demonstrated a few years ago by Szwarc (1989). Besides the cyclic product, linear chain extension products characterized by much higher average molar masses than the precursor are obtained. In addition, the formation of larger rings containing more than one precursor unit cannot be excluded. The presence of such species is still difficult to prove. More recently Dong et al. (1996) extended these calculations to systems where partial deactivation may have occurred.

### 19.2.2.1 End-to-End Cyclization Based on Bimolecular Processes

#### *Cyclic Polystyrenes*

The end-to-end cyclization reaction was first applied to the synthesis of cyclic polystyrenes and proceeds as indicated in Scheme 19-3. Well-defined linear  $\alpha,\omega$ -bifunctional polystyrenes were prepared by anionic polymerization in THF or tetrahydropyran using potassium dihydronaphthylide (potassium naphthalene) as initiator. In a second step, these living polymers were reacted with a stoichiometric amount of a low molar mass bifunctional compound exhibiting antagonist functions such as  $\alpha,\alpha'$ -



**Scheme 19-3.** Schematic representation of the end-to-end cyclization reaction based on anionic polymerization (bimolecular process).

dichloro-*p*-xylene (Geiser and Höcker, 1980)  $\alpha,\alpha'$ -dibromo-*p*-xylene (Hild et al., 1980), or dimethyldichlorosilane (Roovers and Toporowsky, 1983).

These bifunctional, low molar mass, deactivating agents have been selected for their capacity to furnish a quantitative reaction with the carbanions. As discussed previously, this reaction has to be conducted at high dilution in order to favor cyclization rather than chain extension. In spite of the high dilution, the formation of a chain extension product cannot be avoided to a significant degree. Thus the cyclic material has to be isolated from the raw reaction product by fractional precipitation. Owing to the large differences in molar mass between the chain extension product and the cyclic material, the latter can be removed quantitatively. This cyclization procedure was first applied by Geiser and Höcker (1980) and Vollmer and Huang (1980) to synthesize well-defined cyclic structures, but for a limited domain of molar masses. Under these conditions, the properties of long chain cycles could not be studied. Cyclic polymers of molar masses higher than 50 000 g/mol are required to really be able to compare their

solid state properties to their linear equivalent. This cyclization reaction was extended to a larger domain of molar masses by Lutz et al. (1986) up to 200 000 g/mol and by Roovers and Toporowsky (1983) with molar masses up to 450 000 g/mol. Beyond this value, the probability of accidental deactivation is too high to expect cycles free of linear precursor. Even for cyclics of lower masses accidental deactivation may happen, whereby linear chains of the same molar mass are formed. These chains cannot be removed from the cyclic material. It has to be pointed out that the procedure used by Geiser and Höcker (1980) to isolate the cyclic polymers was different: After cyclization, a living, high molar mass polystyrene was added to the reaction product which led to a coupling reaction with the chlorine groups present on the chain extension product, whereas no reaction occurred with the cycle. By redissolution in toluene, the cyclic polymer could be removed by centrifugation. For all these isolated cyclic samples, ultracentrifugation or SEC was used as a first test to check their purity.

Ishizu and Kanno (1996) have taken advantage of the interfacial character of the re-

action conducted between  $\alpha,\omega$ -dibromobutyl PS (dissolved in toluene) and hexamethylene diamine (in water) to obtain well-defined cyclic polymers in almost quantitative yields.

### *Cyclic Polydienes*

The entanglement molar mass ( $M_e$ ) for linear polydienes, polybutadiene (PB), and polyisoprene (PI) is much lower than for PS. This must be the same, at least to some extent for cyclic species. The upper limit in molar masses accessible is not different from that for PS. Thus the properties of cycle polydienes are accessible over a much larger domain of molar masses. In addition, due to the lower  $T_g$  values of polydienes, the solid state properties are accessible at room temperature. The  $T_g$  strongly depends on the microstructure of the polydiene. Monofunctional polydienes exhibiting high contents of 1,4 units can easily be obtained by anionic polymerization provided lithium is used as a counter ion and the solvent is nonpolar. The preparation of cyclic polydienes implies the availability of efficient bifunctional initiators. This was not the case when Roovers and Toporowsky (1988) started their work in that area. They prepared cyclic PB in polar solvents (THF/hexane) using naphthalene lithium as initiator for the anionic polymerization and dimethyldichlorosilane as the coupling agent. Well-defined cyclic PB could be obtained almost free of linear contaminants, the microstructure being 63%, 1,2, 30% trans-1,4, and 7% cis-1,4. These samples served for the study of the solid state properties discussed later in the text. It has to be mentioned that Fetters claimed many years ago to have prepared cyclic polydienes characterized by a high 1,4-content.

Recently El Madani et al. (1992) worked again along this line. Upon reacting 1,2-

bis(isopropenyl-4-phenyl)ethane (BIPE), acting as a coupling agent, with  $\alpha,\omega$ -dithiopolyisoprenes in hexane solution in the presence of THF (15% in volume) at  $-40$  to  $-50^\circ\text{C}$ , cyclic PI is generally obtained in much higher yields (up to 80%) than for PS. Contrary to the end-to-end cyclization reactions described up until now, the procedure developed by El Madani implied an addition reaction onto a double bond and not a deactivation. This is not in favor of the cyclization. A possible explanation for the higher cyclization yield may be that the active chain ends are intramolecularly associated in nonpolar solvents. This may be in favor of intramolecular coupling. Even if the introduction of THF destroys this association, the new species formed upon addition onto BIPE may still be partially associated. This reaction has been extended to other coupling agents such as  $\text{SiCl}_4$ , which will be discussed later.

### *Cyclic Poly(2-vinylpyridine)s (P2VPs)*

Most of the work in the domain of cyclic polymers by end-to-end cyclization has been devoted to PS. The effect of cyclization on various properties of these PSs has been examined in detail. These studies are still limited to organic solvents as unmodified PS is not soluble in water. In addition, no research has been done in the domain of cyclic polyelectrolytes in spite of the interest of this problem. Poly(2-vinylpyridine)s (P2VPs) are far better candidates for such studies. Toreki et al. (1987) and Hogen-Esch et al. (1991) were the first to apply the end-to-end cyclization reaction to the synthesis of cyclic P2VP. The synthesis of linear P2VP via anionic polymerization is now well controlled. The greater stability of P2VP anions may even favor good achievement of the end-to-end cyclization reaction. Furthermore, P2VP can be quaternized with

alkyl halides giving access to polyelectrolytes. As just pointed out, the properties of linear poly(electrolyte)s are well established, but only a few results exist from the structural studies of cyclic poly(electrolyte)s.

As for PS cycles, the first step of the reaction is the synthesis of living  $\alpha,\omega$ -bifunctional P2VP under the specific conditions required for the controlled anionic polymerization of 2-vinylpyridine (appropriate bifunctional initiator, low temperature, and vapor phase addition of the monomer). Here again, in spite of the high dilution, chain extension and cyclic polymers resulted. Their separation could be achieved by fractional precipitation using trichloromethane as a solvent and hexane as a precipitant. SEC experiments (conducted in THF in the presence of triethylamine) and intrinsic viscometry measurements confirmed the cyclic nature of these species. The solid state properties and especially the glass transition temperature were measured and the values compared to those of linear polymers. This aspect will be discussed later.

### *Cyclic Block Copolymers*

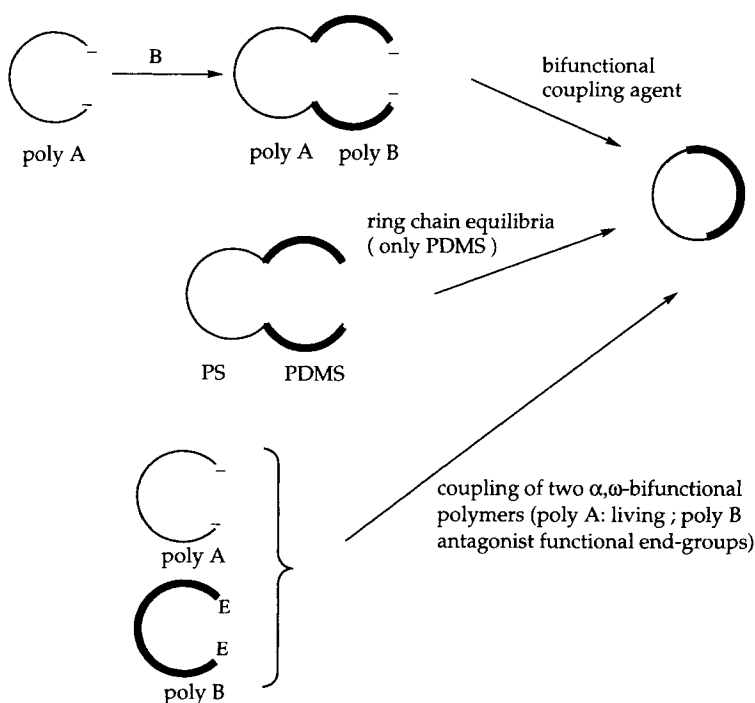
Linear diblock and triblock copolymers have attracted increasing interest over the years, due to the presence of sequences of the same macromolecule of different chemical natures (Riess et al., 1985) leading to specific solution or solid state properties. In the case of cyclic diblock copolymers, the dimensions of one of the sequences may be affected by the cyclization. This aspect was studied theoretically a few years ago by Huber (1988), but the predictions made could not be verified then due to the absence of appropriate materials.

In the solid state, the arrangement in microdomains may also be different from the linear equivalent. The explanations introduced for the microdomain dimensions of

linear diblock or triblocks may not be valid anymore; this has been discussed theoretically by Leibler (1980). The preparation of linear diblock or triblock copolymers with blocks whose lengths are well-controlled requires the application of anionic polymerization. The active sites present at the one or two chain ends can be used to efficiently initiate polymerization of the second monomer.

Jones (1974) first mentioned the synthesis of cyclic block copolymers.  $\alpha,\omega$ -Bifunctional living PSs were prepared first via anionic polymerization followed by the addition of  $D_3$ . After appropriate deactivation, these linear triblock PDMS-*b*-PS-*b*-PDMS were reacted with potassium hydroxide to obtain cyclic copolymers in the presence of diglyme as a promoter. Even if this cyclization reaction could not be quantitatively achieved, these experiments have demonstrated the feasibility of such cyclic diblock structures.

Better results concerning the synthesis of cyclic polymers containing block copolymeric sequences have recently been obtained. Yin and Hogen-Esch (1993) and Yin et al. (1994) first prepared cyclic PS/PDMS block copolymers and then extended the synthesis to cyclics exhibiting P2VP sequences (Gan et al., 1994). General strategies to synthesize block copolymeric cycles are presented in Scheme 19-4. They have been presented in the different articles cited above and will therefore not be discussed here. The efficiency of each approach is directly related to the nature of the different blocks of the copolymer. The preparation of cyclic block copolymers of ethylene oxide and butylene oxide also has to be mentioned, as it refers to a different approach for the synthesis: A triblock copolymer containing a central butylene oxide block and terminal ethylene oxide blocks is reacted with dichloromethane under Williamson conditions.



monomer A : styrene

monomer B : D<sub>3</sub> D<sub>4</sub>, 2-vinylpyridine, dienes, oxirane

**Scheme 19-4.** General strategies for the synthesis of macrocyclic block copolymers.

The obtained cyclic copolymers are especially designed for their specific associative properties (Yu et al., 1996). Beniat et al. (1996) have also developed a new strategy for preparing semicyclic amphiphilic diblock copolymers, which will be discussed later.

### Cleavable Cycles

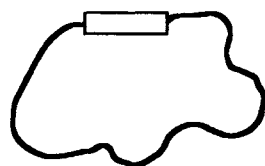
Schober and Gordon (1994) have recently discussed the preparation and characterization of efficient bifunctional initiators containing cleavable bonds. They have extended the use of these initiators to the synthesis of cyclic PS by appropriate deactivation of bifunctional precursors (Fig. 19-2 a). The major advantage of such species lies in the fact that after hydrolysis it should be


possible to have access again to the linear precursor. It also has to be mentioned that Schober and Gordon developed a nice way to isolate the cyclic polymer. The raw reaction product is treated with a living monofunctional P2VP to ensure coupling reactions with the electrophilic groups present at the chain ends of the chain extension product. The cyclic material, PS, does not react and is extracted from the cyclohexane solution due to its good solubility.

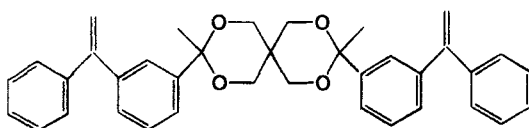
### Reversible Cyclization

Cyclic structures generally imply the presence of a covalent linkage point originating from irreversible coupling of both the macromolecule's chain ends. In the example of a cyclic species containing a cleav-

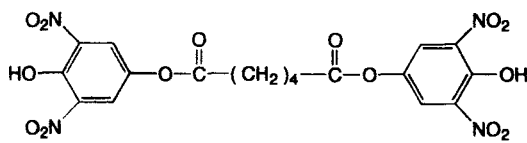




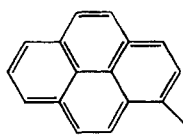
 can be: a or b or c



a



b



c

**Figure 19-2a, b, and c.**  
Cyclic structures containing reversible linking points in the chain

able bond, which has just been discussed, this bond originates from the initiator itself. Association of a macromolecule's two ends constitutes another approach to obtain non-permanent cyclic structures.

Merkle and Burchard (1992) were pioneers in this domain. They studied the associating coupling process of tertiary-amino-terminated polystyrenes with bifunctional dinitrophenol derivatives (Fig. 19-2b). This reaction was followed by UV spectroscopy. Coupling of the functional polymers, i.e., the chain extension and the ring closure, was followed by light-scattering methods. The results were compared to theoretical predictions: The increase of the molar masses was in good agreement with Flory's theory (Flory, 1953), and Jacobson–Stockmayer calculations were applied to determine the amount of rings formed. Reversible cycliza-

tion can also be achieved using polymers (PS) fitted at both chain ends with pyrenyl groups and able to form intramolecular excimers upon electronic excitation of the chromophore (Fig. 19-2c) (Li et al., 1983; Martinho et al., 1995).

One of the major advantages of the synthesis of cyclic structures by end-to-end cyclization reactions is due to the fact that the molar mass of the precursor chain for the potential cyclic can be controlled in advance. Generally, the cyclization results directly upon deactivation of the living chain ends.  $\alpha,\omega$ -Well-defined bifunctional polymers are also designed as good candidates to prepare well-defined cyclic polymers. Polymers fitted with hydroxyl functions are specially designed for such reactions. Poly(ethylene oxide) constitutes an excellent candidate for end-to-end cyclization. In

spite of the interest in cyclic PEO as an example for studying the influence of its cyclic structure upon crystallization, only a little work has been done in this area. The classical end-to-end cyclization reaction was first applied more or less efficiently to the synthesis of PEO cycles. Other approaches were developed which were more successfully directed to well-defined, commercially available polymers fitted with hydroxyl functions at both chain ends. PEO was reacted with dichloromethane under appropriate conditions (Williamson reaction), which provided access to cyclic PEO. Separation of the cyclic polymer from the raw reaction product is still difficult, due to the uncontrolled "cooperative" crystallization of the different species. Ishizu and Akiyama (1997) were able to improve this cyclization procedure when they took advantage of Williamson reactions, conducted in a heterogeneous medium at the interface, to prepare almost quantitatively cyclic PEOs.

Along the same line, the study of the influence of cyclization on the configuration and conformations of semicrystalline polymers such as polyethylene has to be mentioned. The synthesis and isolation of pure cyclic alkanes still represent a major difficulty. Lee and Wegner (1985) were among the first to succeed in the preparation of well-defined cyclic alkanes up to  $C_{288}H_{576}$ . This reaction involved selective oxidation of  $\alpha,\omega$ -diacetylenyl alkanes with copper salt. Under dilute conditions, high yields of macrocyclic species of increasing dimensions could be reached, but had to be chromatographically isolated. The cycloalkanes are finally obtained upon catalytic hydrogenation. Their characteristics, i.e., crystallization, conformation, chain folding, and chain packing, were examined by appropriate methods in direct relation with the number of alkane units incorporated in the cycle (Lee et al., 1987).

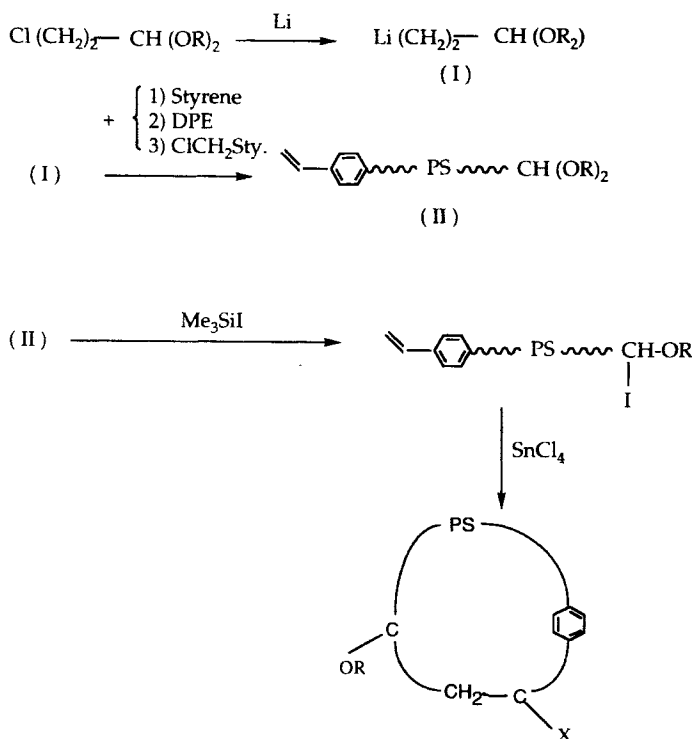
Cyclic hydrocarbons resulting from metathesis reactions were discussed a few years ago by Reif and Höcker (1984).

### 19.2.2.2 End-to-End Cyclization Based on Unimolecular Processes

Most of the cyclic structures obtained by end-to-end cyclization are based upon the reaction of an  $\alpha,\omega$ -bifunctional living polymer with a low molar mass bifunctional compound exhibiting antagonist functions. The first step, the preparation of the functional polymer, refers to anionic polymerization. To reach reasonable cyclization yields, this process has to be conducted at high dilution. This does not favor high yields for the first step of the cyclization reaction, which is the bimolecular reaction of one of the living polymers' active chain ends with one function of the cyclization agent, giving access to the heterofunctional polymer. Thus the reaction between the remaining active chain end and the second antagonist function occurs inter- or intramolecularly. The synthesis of linear polymers exhibiting potential antagonist functions on the two ends of the same chain constitutes the prerequisite. Schappacher and Deffieux (1991) were pioneers in this area. They first applied this principle to the preparation of macrocyclic poly(2-chloroethyl vinyl ether)s (PCEVEs) (Schappacher and Deffieux, 1991), and thus extended the reaction to the case of PS (Rique-Lurbet et al., 1994). Similar systems could be used to design multicyclic polymers, which will be discussed in the final section of this work.

#### *Cyclic Polystyrenes*

The preparation of cyclic polymers based on unimolecular processes implies first the synthesis of a heterobifunctional polymer of well-defined molar mass controlled in ad-



Source: Rique - Lurbet et al, 1994

**Scheme 19-5.** Reaction scheme for the synthesis of polystyrene cycles by unimolecular processes (Rique-Lurbet et al., 1994).

vance and exhibiting two different potential antagonist functions at the chain ends. This was first shown in the domain of cationic polymerization, as discussed later in the text. A quite similar strategy can be used for the preparation of heterodifunctional polystyrenes. The reaction scheme had yet to be adapted to the case of anionic polymerization of styrene (Scheme 19-5). The living anionic polymerization of styrene was initiated by 3-lithiopropionaldehyde diethylacetal. This initiator could be prepared from the chlorine compound by reaction with lithium. After polymerizing styrene under normal conditions, 1,1-diphenylethylene (DPE) is introduced as an intermediate to reduce the reaction of the active chain end, whereupon 4-(chloromethyl)styrene is added under conditions to ensure quantita-

tive incorporation of the styrenyl group. The characteristics of the polymer were in good agreement with expectations. Thus the acetal end groups could be transformed quantitatively in  $\alpha$ -iodo esters by reaction with trimethylsilyliodo ethers. In a terminal step, the cyclization could be performed by the addition of  $\text{SnCl}_4$  in toluene under high dilution conditions. The cyclic nature of the products was confirmed. It has yet to be mentioned that the cyclization yields are lower than expected. This could be explained by a limited stability of the  $\alpha$ -iodo ether end group. In the search for better control of the cyclization, it has been attempted to react the acetal end group directly in the presence of  $\text{SnCl}_4$ , whereby the acetal end group may be directly converted into an active group. The resulting raw polymer was

examined by SEC and almost no chain extension product could be detected.

*Cyclic Poly(2-chloroethyl vinyl ether)*  
(PCEVE)

Among the different monomers that are cationically polymerizable, vinyl ethers have been shown to exhibit a truly living polymerization with all its advantages. Schappacher and Deffieux (1991) have used this polymerization procedure to synthesize heterodifunctional PCEVE. The living PCEVE oligomer or polymer is first prepared with the polymer chain bearing a styrenyl group. That group remains unreacted during the cationic polymerization of vinyl ethers (initiator HI and mild acid conditions). In a second step, intramolecular cyclization is achieved.

In conclusion, the unimolecular process applied to the synthesis of cyclic polystyrenes has proven to be much more efficient than the now classic end-linking process based on the bimolecular process.

## 19.3 Properties of Cyclic Polymers

### 19.3.1 Dilute Solution Properties

#### 19.3.1.1 Size Exclusion Behavior

Once cyclic polymers have been isolated from the chain extension product by fractional precipitation, they have to be submitted for SEC characterization in order to confirm first, as far as possible by SEC, the absence of linear chains of higher molar mass. Thus the cyclic nature of these species can be verified, at least to a first approximation, by a comparison of their elution volume with the linear equivalent's. Special emphasis was given to the SEC study of well-defined cyclic PDMS or cyclic PS. In the lat-

ter case, the cyclic and linear equivalent are accessible in the same synthesis, which is of major importance for a proper comparison of both. This SEC study has been performed systematically by Roovers and Toporowsky (1983). They have established an universal calibration relationship ( $M_{\text{ring app}} = 0.71 M_{\text{ring real}}$ ) which is valid for a large range of molar masses. It has to be mentioned here that the absence in the cyclic samples of chain extension products or other species of higher molar mass, i.e., of double cycles, could be confirmed by light-scattering measurements: The molar masses of the cyclic and linear precursor corresponded exactly.

#### 19.3.1.2 Limiting Viscosity Numbers

For these different samples, the limiting viscosity numbers were measured for the cyclic and its linear equivalent in a theta solvent as well as in good solvents. The values obtained in theta solvents for cyclic PDMS by Dodgson and Semlyen (1977) and for cyclic polystyrenes by Geiser and Höcker (1980), Roovers (1985a), Lutz et al. (1986), and Zhang and He (1991), or for polybutadienes by Roovers and Toporowsky (1988) were found to be in good agreement with the expected values published many years ago. A value of 0.658 was obtained by Bloomfield and Zimm (1966), Fukatsu and Kurata (1966) found 0.645, and Berry and Casassa (1970) calculated 0.66 under theta conditions. More recently, Huang et al. (1986) and Qian and Cao (1987) theoretically re-examined the intrinsic viscosity behavior and the results obtained are generally independent of the molar mass of the cyclic polymer. Some discrepancies are observed with data indicated in the literature. The values given in a preliminary article by Hild et al. (1983) showed the ratio to increase with molar mass. This result has to be attributed to

the presence of high amounts of linear precursor, resulting from deactivation during the cyclization procedure. This precursor could not be removed by fractional precipitation and was not detected by SEC. The case of the high molar mass cyclic prepared by Roovers and Toporowsky (1983) and Roovers (1985a) is much more interesting. The ratio is generally by 0.60, slightly lower than the expected value. It is necessary to be aware of the fact that these samples have been synthesized under theta conditions. The problem has been discussed recently by De Gennes (1990). In order to confirm these results, cyclic polystyrenes have been prepared on purpose under limited solubility conditions. The characterization of these samples is now in progress (Lutz et al., in preparation). Intrinsic viscosity measurements have also been conducted in a good solvent. In contrast to theta solvents, the ratio seemed to slightly increase with the molar mass of the cyclic polymer (Geiser and Höcker, 1980).

### 19.3.1.3 Thermodynamic and Hydrodynamic Properties

The mean square radius of gyration of a cyclic polymer in a theta solvent is expected to be exactly half that of a linear homolog of the same molar mass. Due to the rather limited molar masses of the different well-defined cyclic polymers (PDMS, PS molar masses <400 000 g/mol), a precise determination of the mean square radius of gyration is not possible by light-scattering techniques. Some preliminary results have, however, been obtained by Roovers on high molar mass PS. Accurate measurements for a large range of molar masses resulted from small angle neutron scattering (SANS) measurements. As expected from the theory, the  $R_g$  values of cycles are smaller by a factor of two than those of the linear equiv-

alent. These results were found for PS or PDMS cycles, generally under theta conditions, and there is good agreement between the different groups working in this area (Higgins et al., 1979; Ragnetti et al., 1985; Lutz et al., 1986; Hadziioannou et al., 1987).

Dynamic properties of cyclic polymers as compared to their linear equivalent were examined by quasi-elastic light or neutron scattering first in dilute solution. The results obtained by Duval et al. (1985) and Hadziioannou et al. (1987) were compared to the theoretical predictions established by Yamakawa (1971). The first order perturbation theory of Fukatsu and Kurata (1966) predicts a ratio of translational diffusion constants ( $D_{\text{ring}}/D_{\text{linear}}$ ) of 1.178, close to the measured value for cyclic PS. Examination of the translational diffusion coefficients for samples of increasing molar mass revealed a slight decrease of the value with increasing molar mass: The ratio is equal to 1.20 for a molar mass of 10 000 g/mol and 1.11 for 180 000 g/mol. No fully satisfactory explanation could be found to account for this result. Similar ratios were obtained by Edwards et al. (1982) for cyclic PDMS, the values being determined in either good or theta solvents. The results were obtained from samples with much more limited molar mass ranges than for PS. The translation diffusion coefficient and the hydrodynamic radii measured for cyclic PS or PDMS were found to be only slightly influenced by the cyclization as compared with parameters such as viscosity numbers and radii of gyration. More recently, Merkle et al. (1993) examined the behavior of cyclic PS in dilute and semi-dilute solution with the aim of determining the influence of the structure on the osmotic moduli. The results were compared to those obtained for linear or star-shaped polymers and to the theoretical predictions.

### 19.3.2 Solid State Properties

The reptation model established and discussed by Edwards (1967) and De Gennes (1971) involves a chain motion process for linear chains along a "curviline" tube formed by the constraints of the surrounding matrix. This model has been tested for linear chains in different linear matrices by Green and Kramer (1986), in networks by Kan et al. (1980), for mixtures of linear polymers by Montfort et al. (1984) and Graessley and Struglinski (1986), and for star-shaped polymers by Toporowsky and Roovers (1986) and Pearson and Helfand (1983). In the latter case, it has been demonstrated that the star-shaped structure prevents reptation due to the presence of core and branches. In cyclic polymers no chain ends are present, thus they cannot reptate in a conventional manner. Klein (1986) has treated the diffusion of cyclic chains in a matrix of linear chains where the motion of the rings is mainly determined by "tube renewal".

The behavior in the solid state of ring polymers in a matrix of cyclic chains has only been examined in a few cases (Mills et al., 1987; Tead et al., 1992). In the latter case, the influence of different topologies on the diffusion properties was studied.

The molar mass dependence of the zero shear melt viscosity of cyclic PS, as shown by Roovers (1985b), Schopp and Vollmert (1985), and McKenna et al. (1987), and for PB obtained by end-to-end cyclization (Roovers, 1988), and cyclic PDMS, as found by Dodgson et al. (1980) and Semlyen (1997), was also investigated for a large range of molar masses encompassing  $M_e$ . This behavior was compared to that of linear chains.

The different results obtained along this line have been the subject of a long debate and only the main conclusions will be presented here.

The data reported by Semlyen on PDMS cycles only concerned measurements for molar masses below or around  $M_e$ . They cannot be used for the study of the evolution of the viscoelastic properties of cycles as compared to linear polymers.

For PS or PB cycles, it is now generally accepted that the melt viscosity of cyclic polymers is more reduced than for the linear equivalent. This result seems to be valid for all molar masses studied and is consistent with the different types of cyclic polymers obtained by end-linking procedures.

The strong increase of the melt viscosity with increasing molar mass can mainly be attributed to the presence of linear chains.

This solid state behavior of cyclic polymers can also be examined by following the evolution of the glass transition temperature ( $T_g$ ) with the molar mass: On the one hand, it is now well established that the  $T_g$  of linear chains (PS) decreases rapidly with decreasing molar mass for  $M$  values lower than 40 000 g/mol. This is explained by the effect of chain ends. On the other hand, theoretical studies (DiMarzio and Guttman, 1987) have shown that the  $T_g$ s for cyclic polymers should be less affected by a decrease of the molar mass.

This problem was first discussed for cyclic PDMS (Semlyen, 1997) and for cyclic P2VP (Hogen-Esch et al., 1991). The data reported by the two authors are consistent: above 40 000 g/mol, no difference in  $T_g$  is observed when compared to linear samples.

For lower molar masses, the  $T_g$  is higher and even seems to increase with decreasing molar mass. A  $T_g$  difference of 40°C was observed for cyclics with a degree of polymerization,  $DP_n=40$  in comparison to the linear equivalent. According to the entropy theory of glasses, DiMarzio and Guttman (1987) attributed the increase of  $T_g$  of cyclic polymers of low molar masses as com-

pared to the linear equivalent to an increase of the conformational stiffness.

Gan et al. (1995) have recently taken this problem up again. They concluded that the presence of contaminant in the cyclic polymers (such as LiCl) affects the  $T_g$  value much more than cyclization. The difference in the  $T_g$  for linear and cyclic polymers is much less important for cyclics absolutely free of LiCl. The effect previously claimed by Hogen-Esch could be explained by coordination of one or two pyridine to the lithium cation.

Cyclic diblock copolymers (PS-*b*-PDMS, PS-*b*-2VP) have also been examined regarding their morphologic behavior by Lescanec et al. (1995).

## 19.4 Structures Derived from Cyclic Polymers

As mentioned in the introduction, the synthesis and study of cyclic polymers is essentially caused by the request for well-defined structures specially designed for comparative studies between experimental behavior and theoretical expectations. Much effort has been devoted to the development of efficient preparation methods to access such structures. Cyclic homo and copolymeric species exhibiting different chemical natures and with large ranges of molar mass have been synthesized and characterized properly. These studies only dealt with monocycles. The presence of cyclics containing two or more precursor chains cannot be entirely excluded in these reactions. The synthesis of such structures will be discussed below. Even though the complexity of such macromolecules does not allow precise characterization to confirm the expected structure, the synthesis of such species is driven by the beauty of chemistry.

### 19.4.1 Eight-Shaped Polymers

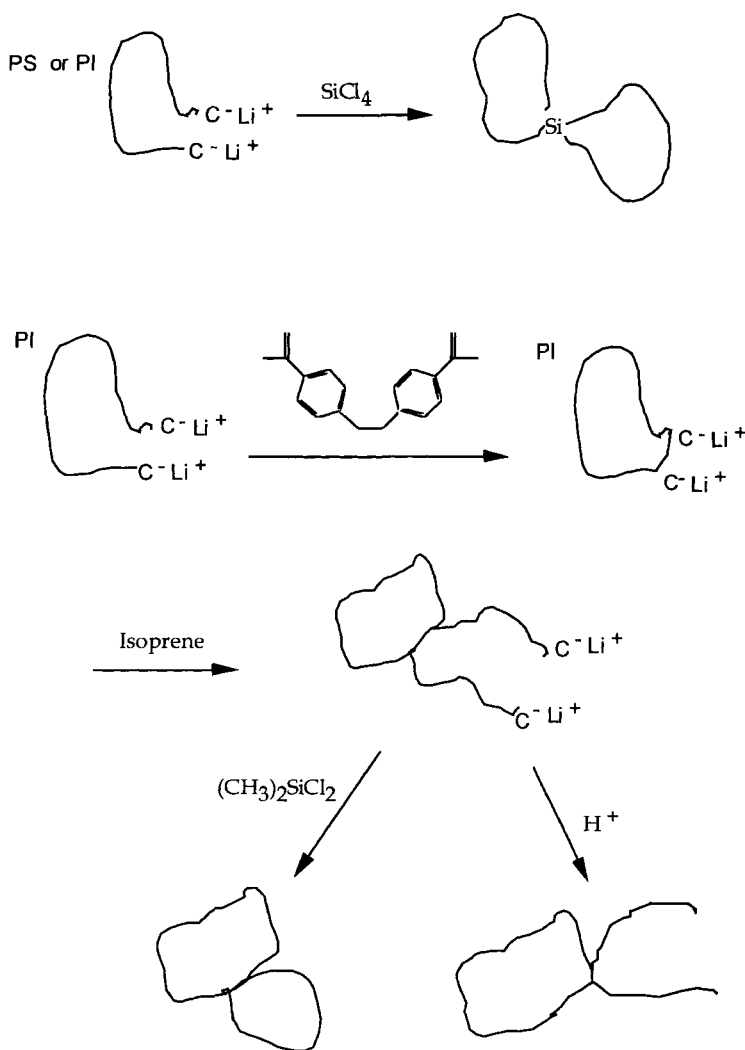
Back-biting implies the reaction of a function located at the chain end with one located along the chain, whereby cyclic species are obtained. Grafting onto functions located along the chain may provide access to a new macromolecular architecture: a linear chain to which a cycle is attached. Beinart et al. (1996) have taken advantage of this approach in their unimolecular cyclization reactions. The first step is the preparation of a linear  $\alpha$ -acetal  $\omega$ -styrenyl vinyl ether-*block*-styrene polymer. A functional group, located in the central part of the polymer backbone, between the PS and the PCEVE sequences is reacted with the terminal vinyl group and furnishes the target structure.

Along the same line, Schappacher and Deffieux (1992) developed the synthesis of heterohexafunctional species based on three functions designed to initiate the cationic polymerization of CEVE and three styrenyl functions. Here again, upon reaction between the activated terminal group of the PCEVE chain and the styrene group, cyclic structures are formed. The hexafunctional nature of the initiating core enabled the synthesis of multicyclic structures where three cycles are present on the same core. Such species have been recognized for their potential to exhibit host–guest properties.

Dimethyldichlorosilanes or bromomethylbenzenes have proved their efficiency in the preparation of cyclic structures. The search for efficient deactivating agents in the synthesis of star-shaped polymers has shown that under specific conditions only two functions of  $\text{SiCl}_4$  may react with  $\omega$ -functional living polymers. Provided  $\alpha, \omega$ -living polymers are reacted under appropriate conditions, cyclic structures containing two unreacted chlorine functions may be obtained. More interesting is the reaction of these living bifunctional polymers with the

four functions of  $\text{SiCl}_4$ , whereby eight-shaped polymers should be accessible. Antonietti and Flösch (1988) were the first to work along this line. They showed that the reaction of  $\alpha, \omega$ -living polystyrenes with  $\text{SiCl}_4$  gives access to well-defined eight-shaped polymers in rather satisfactory yields (Scheme 19-6). A quite similar strategy was developed by El Madani et al. (1992) to synthesize eight-shaped polyisoprenes (Scheme 19-6). The living polymer was directly reacted with  $\text{SiCl}_4$ . Alterna-

tively, the tetrafunctional compound was replaced by 1,2-bis(isopropenyl-4-phenyl)ethane for the first step followed by reinitiation of the polymerization of isoprene and deactivation with dimethyldichlorosilane. Scheme 19-6 compares these different approaches. Schappacher and Deffieux (1995) utilized the unimolecular cyclization process to prepare similar species by reacting two activated functions located at the chain end with two central antagonist functions.



**Scheme 19-6.** Reaction schemes for the preparation of eight-shaped polymers.



### 19.4.2 Catenanes and Rotaxanes

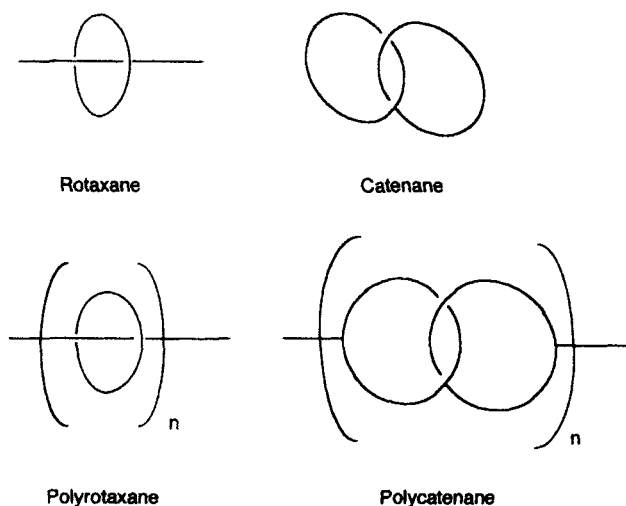
The examples of multicyclic structures just mentioned imply the existence of permanent covalent links connecting the two cyclic structures. The two cycles cannot freely rotate about each other as in catenanes (Fig. 19-3). The synthesis of not chemically but physically linked catenanes represents a major challenge for chemists. One possible approach to macromolecular catenanes could be to apply the end-to-end cyclization reaction based on ionic polymerization. Provided the end-to-end cyclization reaction is conducted in the presence of an already existing cyclic compound, catenanes may be obtained by threading the linear macromolecule through the cycle followed by cyclization. Rempp (unpublished results) has applied this strategy to the synthesis of PS macromolecular catenanes. The efficiency of this method is, however, questionable. Even if such species existed, isolation from the raw reaction product would remain a major difficulty.

The first investigation demonstrating the feasibility and the existence of catenanes was published at the beginning of the cen-

tury. It is beyond the framework of this chapter to describe all the catenane syntheses published since then, but the reader is referred to some excellent review articles.

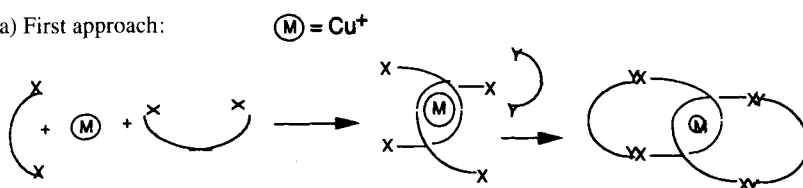
Dietrich-Buchecker et al. (1993) developed a nice method for preparing catenanes. They used the template effect of a transition metal ion to organize ligands in a predictable geometry, one which is ideal for subsequent ring closure. As indicated in the reaction shown in Scheme 19-7, bifunctional low molar mass compounds with functional groups at the chain ends and a central potential linking point were prepared first. Two strategies were developed, the basic principle remaining the same: coordination of a chain fragment containing a central phenantroline derivative which can be linked reversibly with the help of metal ion such as copper (I).

Two functionalized chains with a central phenantroline group are coordinately bound together. Then the terminal functional groups are connected with one another so that the catenane is formed. The major limitation of this reaction is the efficiency of the second step in which not only the intramolecular reaction has to be favored over

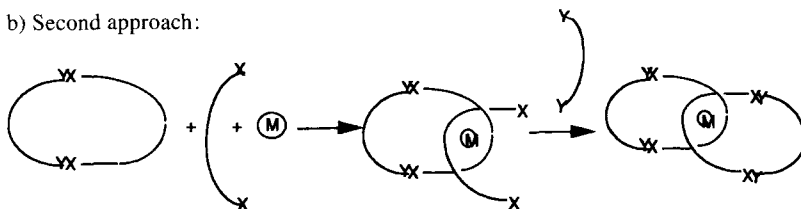


**Figure 19-3.** Multicyclic structures: rotaxane and catenane, polyrotaxane and polycatenane

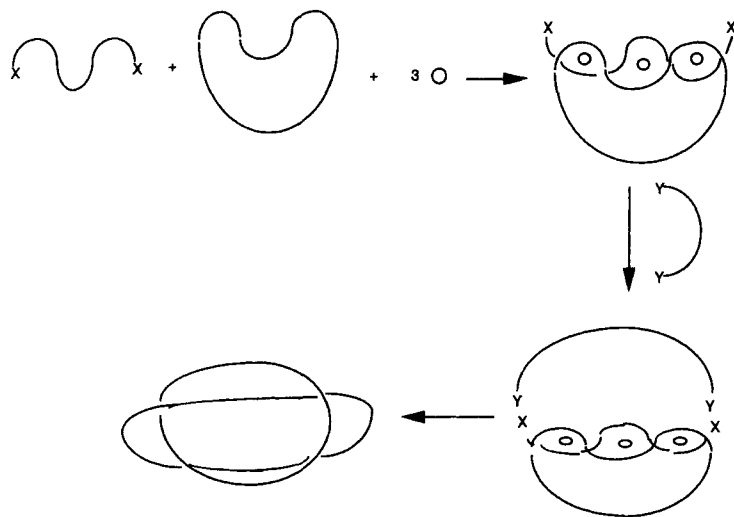
a) First approach:



b) Second approach:



c) Interlocked catenanes



**Scheme 19-7.** Schematic representation of the strategies for the synthesis of catenanes [a, b) Dietrich-Buckecker et al. (1993), c) Nierengarten et al. (1994)].

the intermolecular one, but where only one of the two existent intramolecular paths leads to the desired product.

The second approach consists initially of intramolecularly linking two bifunctional chains, one of which contains the phenantroleine group. Once the cyclic has been obtained, a new bifunctional chain containing a central coordinating fragment is threaded through the first cycle in the presence of copper so that the second cycle is formed resulting again in the expected catenane.

In both cases, catenanes are obtained in good yields provided there is an appropriate combination of metals, chelates, and coupling chemistry. Template effects have also been developed by Ashton et al. (1989) to prepare catenanes.

The method has been extended by Nierengarten et al. (1994) to design doubly interlocked [2] catenanes. Basically (see Scheme 19-7), two kinds of species have to be prepared first: molecule A containing three chelating molecular fragments and a

cycle containing the corresponding complexing fragments. The two compounds are mixed together in the presence of the appropriate metals. In a final step the ring closure reaction is conducted and the expected structure is obtained.

Catenanes, due to the originality of their structure, have attracted increasing interest over the years. The present work has only discussed a limited number of examples. A more detailed study on the synthesis and properties of such catenanes has recently been published by Sauvage (1990) in a review on cyclic polymers and in Semlyen's book (1997). Structures based on catenanes always imply the presence in the molecule of two cycles not linked together. An increase in the number of units leads to a species called polycatenanes (Fig. 19-3). An example of rigid poly ([2]-catenanes) has been discussed recently by Muscat et al. (1997).

Cyclic polymers can also be used to build up structures such as rotaxanes where a cycle surrounds a linear chain (Fig. 19-3) or polyrotaxanes where more than one cycle surrounds a linear chain (Fig. 19-3). To access these structures two ways are possible: the so-called statistical approach and the use of template chemistry.

In these rotaxanes no covalent link exists between the linear chain and the cycle, but reversible reaction or coordination between that linear chain and the cyclic is required to build up such structures. The reader is invited to consult the review articles published by Gibson et al. (1994) and Gibson (1997).

The so-called statistical threading method refers to a mixture of cyclic macromolecules with a linear chain. This procedure generally leads to a mixture of rotaxanes and polyrotaxanes, as well as unthreaded linear and cyclic material. To some degree the percentage of cyclics on the chain can be con-

trolled by the stoichiometry of the initial components, the size of the cyclic polymer, and the temperature. The macrocycle yield on the rotaxane remains low. In addition, the polyrotaxane's chain ends have to be blocked by the appropriate bulky molecules to avoid dethreading.

The second approach has been applied by Diederich et al. (1995) to synthesize polyrotaxanes. To prevent dethreading of the cycle they have introduced bulky groups such as fullerenes at the chain ends of the linear macromolecules. Another good example is the use of cyclodextrines (Harada et al., 1992, 1996; Wenz, 1994) in the construction of these architectures.

## 19.5 Conclusions

Much attention has been devoted over the years to the preparation of well-defined cyclic macromolecules. Back-biting reactions provide access to such species in a rather simple way. A great number of polymers are designed for these reactions and have been extensively used in the preparation of macrocycles and their properties, but complete control of the cyclics' characteristics and properties is still impossible. In addition, only a limited number of monomers and linear polymers lead to high molar mass cycles. Furthermore, ring chain equilibrium reactions cannot be applied to vinyl monomers, which limits this otherwise useful method. The end-to-end cyclization method based on ionic polymerization is much more efficient. Combined with the appropriate separation procedures, this method has had considerable impact on the development of cyclic polymer research. Well-defined cyclic polystyrene, polydienes, poly(2-vinylpyridine), and even cyclic copolymers are now available for a large range of molar mass. The properties of all

these different cycles could thus be studied, and it is now clear that they meet with the theoretical predictions made some 40 years ago. The end-to-end procedures based on bimolecular processes have, however, a drawback: Even if the reaction is conducted at high dilution, cyclic and chain extension products are always present together in the reaction medium. The latter has to be removed by fractional precipitation. Deffieux has improved the cyclization procedure. Upon using heterofunctional polymers with narrow molar mass distributions and an appropriate activation of their terminal functional groups, well-defined cycles could be obtained in almost quantitative yields.

These end-to-end cyclization reactions based on either unimolecular or bimolecular processes have opened new perspectives in the domain of macromolecular engineering. Two cases have in particular been examined in this chapter: incorporation and construction of architectures based on real macrocycles and the use of various cycles of lower dimensions to the elaboration of structures designed for specific applications.

## 19.6 References

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